

# Electronic Supporting Information

**Table 1**

	<b>Zn ppm</b>	<b>Zn <math>\mu\text{mol/g}</math></b>	<b>% coordination</b>
<b>12.ZnSO<sub>4</sub></b>	335	5.12	6.0
<b>12.ZnATSMA</b>	539	8.24	9.6
<b>12.ZnX<sub>2</sub></b>	30	0.45	-
<b>12.ZnATSM</b>	203	3.10	3.6
<b>12.ZnX<sub>2</sub></b>	77	1.18	-

The number of pyridine units of polymer **12** is 0.086 mmol/g.

$$Zn(\mu\text{mol} / \text{g}) = \frac{Zn(\text{ppm})}{65.39(\text{g} / \text{mol})Zn}$$

$$\% \text{coordination} = \frac{Zn(\mu\text{mol} / \text{g}) \times \left( \frac{10^{-3} \text{mmol}}{1\mu\text{mol}} \right)}{0.086(\text{mmol} / \text{g})} \times 100$$

## Experimental

### General

<sup>1</sup>H NMR spectra were recorded on Bruker DPX200 (200 MHz) or Bruker DQX400 (400 MHz) spectrometers. Chemical shifts ( $\delta_{\text{H}}$ ) are reported in parts per million (ppm) and are referenced to the residual protonated solvent peak. The abbreviations used to describe multiplicities are as follows: s (singlet), ds (double singlet), d (doublet), dd (double doublet), m (multiplet) and br (broad). Coupling constants (J) are given in Hertz (Hz). Two-dimensional COSY (correlation spectroscopy) spectra were obtained on a Bruker DQX400 spectrometer at 400 MHz. <sup>13</sup>C NMR spectra were recorded on a Bruker DQX400 spectrometer at 101 MHz with proton decoupling. Chemical shifts ( $\delta_{\text{C}}$ ) are reported in parts per million (ppm) and are referenced to the residual protonated solvent peak. Assignment was aided by the use of DEPT editing, HSQC, and HMQC. Infrared (IR) spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer. Absorption maxima ( $\nu_{\text{max}}$ ) are reported in wavenumbers ( $\text{cm}^{-1}$ ) and only selected peaks are reported. Melting points were recorded using a Stuart Scientific SMP1 melting point apparatus in open capillaries and are uncorrected. Low resolution mass spectra ( $m/z$ ) were recorded on a Fisons Platform spectrometer using electrospray ionisation (ESI). High resolution mass spectra (HRMS) were recorded on a Bruker microTOF (ESI). The  $m/z$  values of major peaks are reported in Daltons and their intensities given as percentages of the base peak. Thin layer chromatography (TLC) was performed using Merck aluminium foil backed sheets precoated with 0.2 mm Kieselgel 60 F<sub>254</sub>. Product spots were visualised by quenching of UV fluorescence ( $\lambda_{\text{max}}$  254 nm), iodine vapour, or by staining with an aqueous solution of KMnO<sub>4</sub> or a solution of 5% (w/v) phosphomolybdic acid in ethanol, followed by heating. Both dips were prepared according to literature methods<sup>1</sup>. All reactions were carried out in oven-dried reaction flasks. 'Petrol' refers to that fraction of light petroleum ether boiling at 40-60 °C and was used as received. Solvents were evaporated at 40 °C or below under reduced pressure on a Buchi RE111 Rotavapor attached to a Vacuubrand CVC2 pump and pressure control system. All reagents were obtained either from Aldrich Chemicals Ltd or Lancaster Chemicals Ltd or Alfa Aesar Chemical Ltd and used as supplied. Reaction times are recorded in hours (h) and minutes (min). Temperatures below 25 °C were obtained using ice/water baths. Surface analysis by Attenuated Total Reflectance Infrared (ATR-IR) was carried out using a Bio-RAD FTS-6000 FT-IR Spectrometer fitted with DuraSamp1IR Diamond ATR. All spectra were recorded at RT. NBS was purified according to the literature method before use.<sup>2</sup> Polystyrene (PS) beads were purchased from Sigma-Aldrich Chemicals Ltd, Amberlite® XAD4 (20-60 mesh, surface area 725 m<sup>2</sup>g<sup>-1</sup>). The synthesis of compounds **1** and **2a-c** was achieved according to the literature method.<sup>3</sup> ZnAT SMA

was supplied by Dr M. Christlieb and ATSM and ZnATSM were prepared according to literature methods.<sup>4</sup>

## Synthesis

### **General Method (I): H-Acid test for presence of diazonium functionality.**<sup>5</sup>

H-acid (4-amino-5-hydroxynaphthalene-2,7-disulfonic acid) was dissolved in water to achieve a beige opaque solution (approximately 1:2 H-acid:water, v/v). The pH of a sample of the diazonium salt solution was adjusted to 4 using NaOAc. The solution was then added to the H-acid solution which was then agitated to ensure thorough mixing. The solution was left for 5min for the colour to develop. A positive H-acid test was observed as a significant colour change from beige to purple resulting from surface reaction of the diazonium compound.

### **General method (II): Functionalisation of polystyrene beads.**<sup>5</sup>

The appropriate diaryldiazomethane (5 mg) was dissolved in ether or THF (5 ml). Amberlite XAD-4 polymer (100 mg) was then placed in the solution and the solvent removed *in vacuo* at RT. This sample was carefully heated in an oil bath at 120°C. When no pink colour, due to diaryldiazomethane, was observable on the appropriate sample, heating was stopped and the sample was washed with excess of acetone until no colour was seen to be washed out.

### **General method (III): Coupling of diazonium compounds on modified polystyrene beads.**<sup>5</sup>

Functionalised Amberlite (100 mg) was treated with a suspension of diazonium salt (12 mg) in water was added and left overnight to stand. Each sample was then carefully washed with water and acetone by filtration through sintered funnel. This process was repeated until no colour was seen to be washed out and final samples were kept for analysis.

### **General method (IV): Metal ion coordination on modified polystyrene beads.**<sup>5</sup>

Each portion of functionalised Amberlite (100 mg) was placed in a separate flask and a solution of ZnSO<sub>4</sub>·7H<sub>2</sub>O (0.5 mg of Zn<sup>2+</sup>/mL, 2 eq) in 1:1 water:acetone was added and left overnight to stand. Each sample was then carefully washed with water and acetone by filtration through sintered funnel.

### **Metal complex coordination on modified polystyrene beads.**

Each portion of functionalised Amberlite **12** (100 mg) was placed in a separate flask and a solution of **13a** and **13c** (8 mg/mL, 2 eq) in DMF was added and left overnight to stand. Each

sample was then carefully washed with DMF, 1:1 EtOH:saline (0.9 % w/v solution), and acetone by filtration through sintered funnel to give modified materials **12.ZnATSMA** and **12.ZnATSM**.

#### **Transmetallation on modified polystyrene beads.**

Each portion of metal-coordinated Amberlite **12.ZnATSMA** or **12.ZnATSM** (100 mg) was placed in a separate flask and a solution of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (4 mg/mL, 1 eq) in 1:1 EtOH:saline (0.9 % w/v solution) was added and left for 72 h to stand.

#### **Synthesis of benzenediazonium chloride 4a.<sup>6</sup>**

To a stirring brown solution of aniline (50.0 mg, 0.54 mmol) in THF/water (1:1) at 0 °C, a mixture of  $\text{NaNO}_2$  (37.0 mg, 0.54 mmol) and HCl 3M (0.36 mL) in water was added. The reaction was stirred at 0 °C and consumption of the amine was tracked by TLC. The red solution was used reacted on straight after completion.

#### **Synthesis of pyridine-4-diazonium chloride 4b.<sup>6</sup>**

To a stirring colourless solution of N-4-aminopyridine (52.2 mg, 0.53 mmol) in THF/water (1:1) at 0 °C, a mixture of  $\text{NaNO}_2$  (37.0 mg, 0.54 mmol) and HCl 3M (0.35 mL) in water was added. The reaction was stirred at 0 °C and consumption of the amine was tracked by TLC. The yellow solution was used reacted on straight after completion.

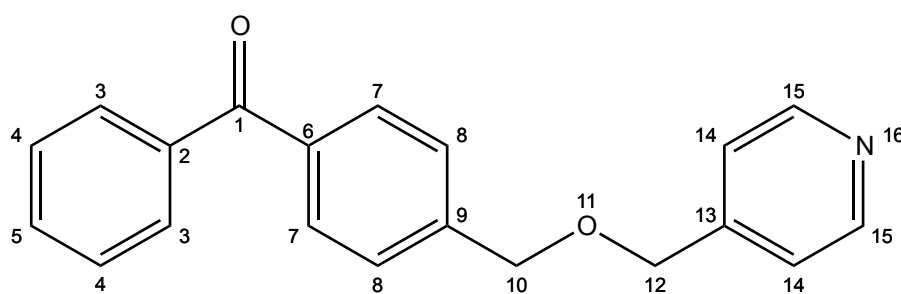
#### **Synthesis of 8-hydroxyquinoline-5-diazonium chloride 4c.<sup>7</sup>**

To a stirring red solution of 5-amino-8-hydroxyquinoline dihydrochloride (50.0 mg, 0.21 mmol) in THF/water (1:1) at 0 °C, a mixture of  $\text{NaNO}_2$  (15.0 mg, 0.22 mmol) and HCl 3M (0.14 mL) in water was added. The reaction was stirred at 0 °C and consumption of the amine was tracked by TLC. The brown solution was used reacted on straight after completion.

#### **Synthesis of 4-((pyridin-4-ylamino)methyl)benzenediazonium chloride 4d.<sup>6</sup>**

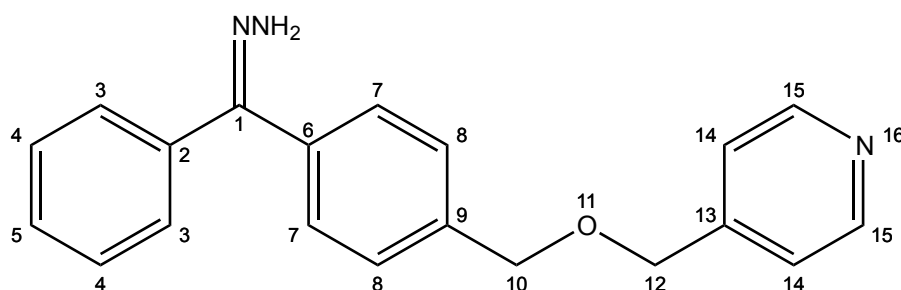
To a stirring yellow solution of N-(4-aminobenzyl)pyridin-4-amine **10b** (111.6 mg) in THF/water (1:1) at 0 °C, a mixture of  $\text{NaNO}_2$  (38.6 mg, 0.56 mmol) and HCl 3M (0.37 mL) in water was added. The reaction was stirred at 0 °C and consumption of the amine was tracked by TLC. The brown solution was used reacted on straight after completion.

#### **Synthesis of phenyl(4-((pyridin-4-ylmethoxy)methyl)phenyl)methanone 6a.**



Pyridin-4-ylmethanol (195.0 mg, 1.79 mmol) and dry THF (5 mL) were added to a pre-purged reaction flask. NaH (122mg, 60% dispersion in oil, 3.05 mmol) was added to the reaction flask and the reaction mixture was stirred at 20°C, for 1h until no more H<sub>2</sub> gas evolution was observed. The solution was heated until the THF boiled using a heat gun. The benzophenone **1** (420.0 mg, 1.53 mmol) was dissolved in THF (5 mL) and was added dropwise to the boiling solution. The reaction mixture was stirred at 20 °C for 48h. The solvent was removed *in vacuo* and the residue was dissolved in DCM, washed with water, dried (MgSO<sub>4</sub>) and the solvent removed *in vacuo*. The crude product was purified by flash column chromatography, eluting with CH<sub>2</sub>Cl<sub>2</sub>:MeOH (9.5:0.5). The product **6a** was obtained as a brown oil (255 mg, 55%):  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  2924, 1656, 1606, 1446, 1413, 1278, 1102;  $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$  8.59(2H, d, J=5.6 Hz, H-15), 7.81(4H, m, H-3 and H-7), 7.61(1H, d, J=7.3 Hz, H-5), 7.46(4H, m, H-4 and H-8), 7.31(2H, d, J=5.6 Hz, H-14), 4.69(2H, s, H-10), 4.62(2H, s, H-12);  $\delta_{\text{C}}(101 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$  196.3(C-1), 149.9(C-15), 147.1(C-13), 142.3(C-9), 137.5(C-2), 137.0(C-6), 132.4(C-5), 130.3(C-3 and C-7), 128.2(C-4 and C-8), 121.7(C-14), 72.1(C-10), 70.7(C-12);  $m/z$  (ESI) 326([M-Na]<sup>+</sup>, 100%), 304([M+H]<sup>+</sup>, 84), 629(2M+Na]<sup>+</sup>, 71); HRMS C<sub>20</sub>H<sub>18</sub>NO<sub>2</sub> requires 304.1338, found 304.1332<sup>7</sup>.

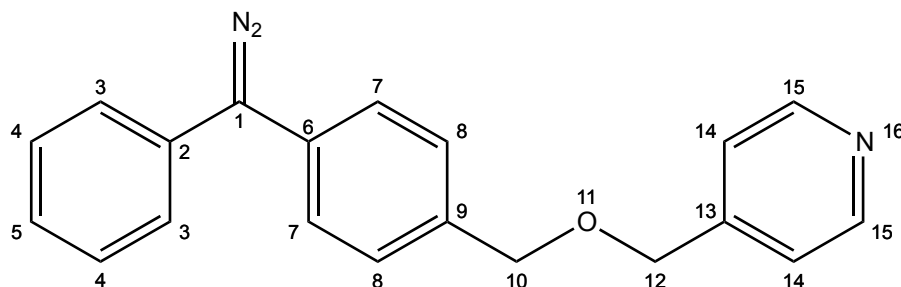
### Synthesis of 4-(((4-(hydrazono(phenyl)methyl)benzyl)oxy)methyl)pyridine **6b**.



The benzophenone **6a** (235.0 mg, 0.77 mmol) was refluxed in EtOH and hydrazine hydrate (1.90 mL, 50.87 mmol) overnight. The solvent was removed *in vacuo* and the residue dissolved in DCM, washed with water, dried and concentrated under vacuum to give 4-(((4-(hydrazono(phenyl)methyl)benzyl)oxy)methyl)pyridine **6b** (244.4 mg, 100%) as a yellow oil. The hydrazone, which was obtained as inseparable mixtures of the syn- and anti- isomers, was then used without further purification:  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3384, 2851, 1606, 1492, 1451, 1416, 1362, 1260, 1099, 800, 699;  $\delta_{\text{H}}(200 \text{ MHz}; \text{CDCl}_3; \text{Me}_4\text{Si})$  8.49(2H, d, J=4.8 Hz, H-15), 7.25-7.55(11H, m, H-3, H-4,

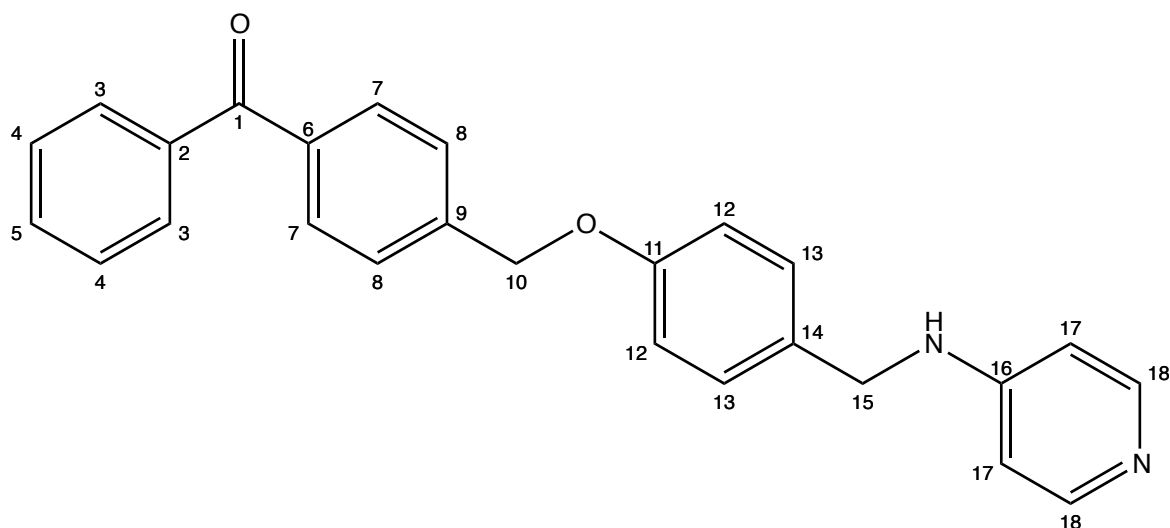
H-5, H-7, H-8, and H-14), 5.44(2H, br s, NH<sub>2</sub>), 4.57(2H, s, H-12), 4.54(2H, s, H-10); δ<sub>c</sub>(101 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 149.7(C-1), 147.6(C-13), 138.4(C-9), 132.8(C-2), 132.5(C-6), 128.9, 128.6, 128.4, 128.1, 127.9, 127.4, 72.5(C-12), 72.4 and 70.2(C-10); m/z (ESI) 326(100%), 304(44), 328(41%), 340([M-H+Na]<sup>+</sup>, 27).

### Synthesis of 4-(((4-(diazo(phenyl)methyl)benzyl)oxy)methyl)pyridine **6c**.<sup>6,8</sup>



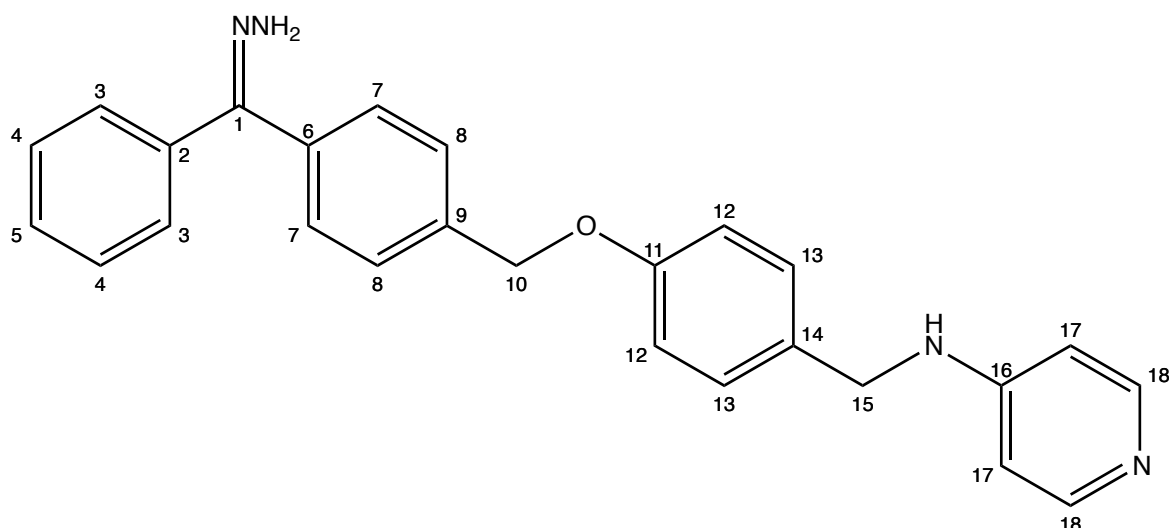
To a mixture of MnO<sub>2</sub> (156.0 mg, 1.80 mmol), Na<sub>2</sub>SO<sub>4</sub> (143.0 mg, 1.01 mmol), and KOH (57.0 mg, 1.02 mmol) in MeOH (5 mL) was added a solution of hydrazone **6b** (190.0 mg, 0.60 mmol) in MeOH (5 mL). The mixture was stirred in the dark for 3h then filtered through a celite pad, and concentrated *in vacuo*. The mixture was extracted with EtOAc, washed with water, dried (MgSO<sub>4</sub>), and then concentrated *in vacuo* to give **6c** (189.2 mg, 100%) as a red oil: ν<sub>max</sub>(film)/cm<sup>-1</sup> 2854, 2039(C=N<sub>2</sub>), 1738, 1605(C=N), 1493, 1416, 1233, 1101, 799, 753, 698; δ<sub>H</sub>(200 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.51-8.55(2H, m, H-15), 7.19-7.42(11H, m, H-3, H-4, H-5, H-7, H-8, and H-14), 4.54(2H, s, H-12), 4.58(2H, s, H-10); δ<sub>c</sub>(101 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 147.5(C-13), 144.0, 143.9, 136.7(C-9), 134.9, 130.3, 130.0, 129.3(C-2), 128.7, 128.4, 127.2, 127.0, 126.8(C-6), 125.7, 121.8, 123.3, 121.8, 72.5 and 70.3(C-10 and C-12); m/z (ESI) 288(100%), 370(97), 328(71), 289([M-N<sub>2</sub>+H]<sup>+</sup>, 45).

### Synthesis of phenyl(4-(((4-((pyridin-4-ylamino)methyl)phenoxy)methyl)phenyl)methanone **7a**.<sup>3</sup>



The phenol **10c** (177 mg, 0.88 mmol) in dry THF (10 mL) was treated with NaH (110 mg, 2.75 mmol, 60% dispersion in oil) and stirred at 20°C for 1h. The bromide **1** (261 mg, 0.94 mmol) was then added and stirring continued for 72h. Excess solvent was removed *in vacuo* and the residue diluted with DCM, washed with water and NaHCO<sub>3</sub> solution (sat.), dried (MgSO<sub>4</sub>) and solvent removed under vacuum to give **7a** as a dark brown semi-solid (347 mg, 100%):  $\nu_{\max}$ (film)/cm<sup>-1</sup> 2923, 1655, 1603, 1510, 1446, 1315, 1277, 1175;  $\delta_{\text{H}}$ (200 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.19(2H, d, J=6.32 Hz, H-18), 7.78-7.84(4H, m, H-3 and H-7), 7.47-7.62(5H, m, H-4, H-5, and H-8), 7.26(2H, d, J=8.59 Hz, H-13), 6.97(2H, d, J=8.59 Hz, H-12), 6.46(2H, d, J=6.32 Hz, H-17), 5.16(2H, s, H-10), 4.29(2H, s, H-15);  $\delta_{\text{C}}$ (101 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 196.2(C-1), 157.9(C-11), 153.0(C-16), 150.0(C-18), 141.5(C-9), 137.5(C-2), 137.1(C-6), 132.5, 130.7, 130.5, 130.4, 130.0, 128.7, 128.3, 126.9, 126.2, 115.1(C-12), 107.1(C-17), 69.4(C-10), 46.2(C-15); m/z (ESI) 395([M+H]<sup>+</sup>, 100%); HRMS C<sub>26</sub>H<sub>23</sub>O<sub>2</sub>N<sub>2</sub> requires 395.1754, found 395.1746.

### Synthesis of N-(4-(4-(hydrazone(phenyl)methyl)benzyloxy)benzyl)aniline **7b**.<sup>3</sup>

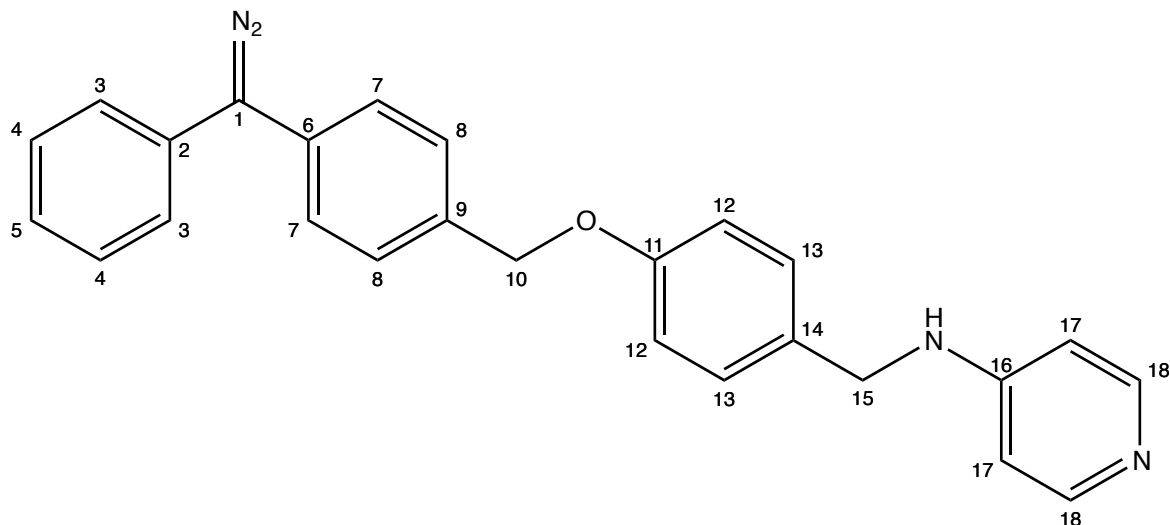


The benzophenone **7a** (810 mg, 2.05 mmol) was refluxed in EtOH and hydrazine hydrate (0.50 mL, 10.31 mmol) overnight. The solvent was removed *in vacuo* and the residue dissolved in DCM, washed with water, dried and concentrated under vacuum to give **7b** (737 mg, 88%) as a dark brown oil. The hydrazone, which was obtained as inseparable mixtures of the syn- and anti-isomers, was then used without further purification:  $\nu_{\max}$ (film)/cm<sup>-1</sup> 3385, 2923, 1650, 1604, 1510, 1444, 1240, 1173;  $\delta_{\text{H}}$ (200 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.14(2H, m, H-18), 6.92-7.84 (13H, m, H-3, H-4, H-5, H-7, H-8, H-12, and H-13), 5.13 and 5.03(2H, dd, J=12.38 and 10.36 Hz, H-10), 4.30 and 4.26(2H, 2s, H-12);  $\delta_{\text{C}}$ (101 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 158.1, 153.2, 149.8, 149.7, 138.2, 137.7, 136.6, 132.8, 132.6, 132.5, 130.4, 130.1, 129.4, 129.1, 129.0, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.5, 127.2, 126.9, 126.4, 115.1, 107.6, 69.7 and 69.6(C-10), 46.2(C-15); m/z (ESI) 409([M+H]<sup>+</sup>,



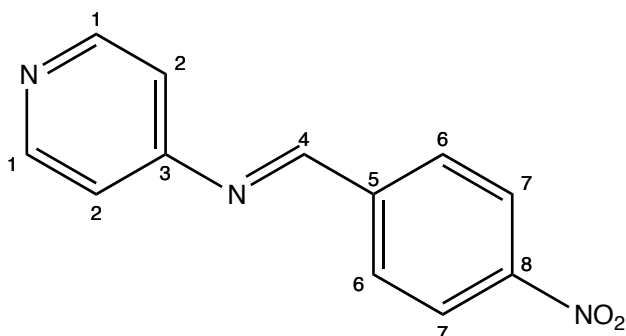
100%), 410(49), 441([M+H+MeOH]<sup>+</sup>, 39); HRMS C<sub>26</sub>H<sub>25</sub>ON<sub>4</sub> requires 409.2023, found 409.2017.

### Synthesis of N-(4-(4-(diazo(phenyl)methyl)benzyloxy)benzyl)aniline **7c**.<sup>6,8</sup>



To a mixture of MnO<sub>2</sub> (474 mg, 5.45 mmol), Na<sub>2</sub>SO<sub>4</sub> (442 mg, 3.11 mmol), and KOH (180 mg, 3.21 mmol) in MeOH (15 mL) was added a solution of hydrazone **7b** (737 mg, 1.81 mmol) in MeOH (15 mL). The mixture was stirred in the dark for 18h then filtered through a celite pad, eluted with EtOAc/Et<sub>3</sub>N, and concentrated *in vacuo*. The mixture was extracted with EtOAc, washed with water, dried (MgSO<sub>4</sub>), and then concentrated *in vacuo* to give **7c** (560 mg, 76%) as a red oil:  $\nu_{\max}$ (film)/cm<sup>-1</sup> 2923, 2039(C=N<sub>2</sub>), 1604, 1510, 1240, 1173;  $\delta_{\text{H}}$ (200 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 8.17(2H, d, H-18), 7.17-7.86(11H, m, H-3, H-4, H-5, H-7, H-8, and H-13), 6.97(2H, d, J=8.6 Hz, H-12), 6.46(2H, m, H-17), 5.06(2H, s, H-10), 4.68(1H, br s, NH), 4.29(2H, s, H-15);  $\delta_{\text{C}}$ (101 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) 158.2(C-11), 153.3(C-16), 149.7(C-18), 134.0, 132.5, 130.4, 130.1, 130.0, 129.5, 129.2, 129.1, 128.7, 128.4, 128.3, 127.5, 127.1, 126.9, 126.8, 126.5, 125.7, 125.2, 125.1, 115.1(C-12), 107.7(C-17), 69.8(C-10), 46.3(C-15); m/z (ESI) 379([M+H-N<sub>2</sub>]<sup>+</sup>, 100%).

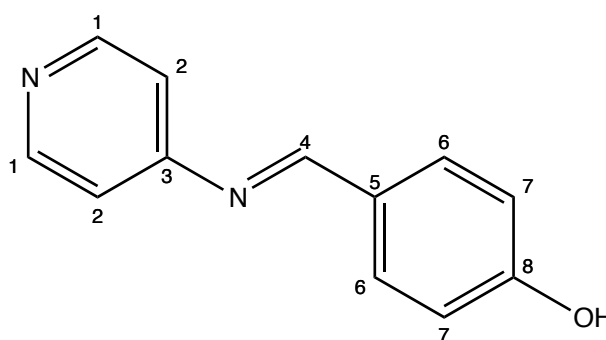
### Synthesis of N-(4-nitrobenzylidene)pyridin-4-amine **9a**.



A mixture of 4-aminopyridine (366.7 mg, 3.90 mmol), 4-nitrobenzaldehyde (587.1 mg, 3.88 mmol), and PPTS (1.20 g, 4.78 mmol) was refluxed in toluene (25 mL) for 18h, during which

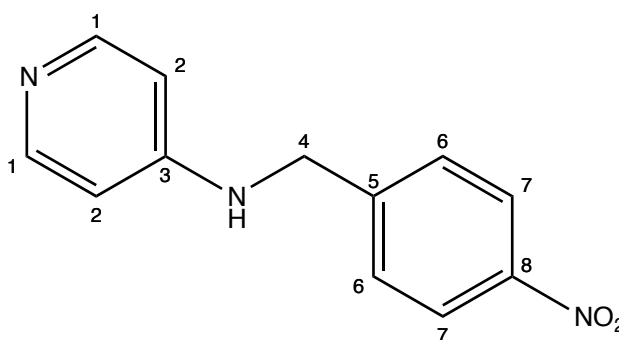
period water was removed periodically by using a Dean-Stark apparatus. The solution was allowed to cool before being concentrated *in vacuo*. The mixture was extracted with DCM, washed with water, dried (MgSO<sub>4</sub>), and then concentrated *in vacuo* to give **9a** (793 mg, 90%) as a yellow solid: mp 110-112 °C;  $\nu_{\max}$ (film)/cm<sup>-1</sup> 3091, 1638(C=N), 1519(NO<sub>2</sub>), 1344(NO<sub>2</sub>), 1204, 1122, 1034, 1011;  $\delta_{\text{H}}$ (200 MHz; CD<sub>3</sub>OD; Me<sub>4</sub>Si) 8.31(2H, d, J=8.6 Hz, H-7), 8.25(1H, s, H-4), 7.86(2H, d, J=8.6 Hz, H-6), 7.68(2H, d, J=8.1 Hz, H-1), 7.22(2H, d, J=8.1 Hz, H-2);  $\delta_{\text{C}}$ (101 MHz; CD<sub>3</sub>OD; Me<sub>4</sub>Si) 157.9(C-3), 140.7, 128.8(C-2), 128.7(C-6), 125.9(C-1), 124.4(C-7), 123.2(C-4); m/z (ESI) 322(100%), 260([M+H+MeOH]<sup>+</sup>, 89), 228([M+H]<sup>+</sup>, 39).

### Synthesis of (E)-4-((pyridin-4-ylimino)methyl)phenol **9b**.<sup>9</sup>



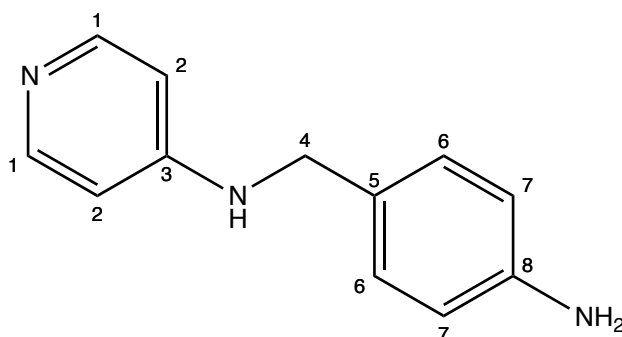
4-Aminopyridine (617 mg, 6.56 mmol) was added to 4-hydroxybenzaldehyde (803 mg, 6.58 mmol) in toluene (20 mL) and then refluxed for 18h. A Dean-Stark apparatus was used for continuous removal of the water that was produced in the reaction. The precipitate formed was washed with hot toluene, dissolved in hot EtOH, then filtered while being hot. The solvent was then removed *in vacuo* to afford **9b** (885 mg, 68%) as a yellow solid:  $\nu_{\max}$ (film)/cm<sup>-1</sup> 3418, 3005, 2918, 2360, 2341, 1651, 1437, 1407, 1316, 1021, 953, 707, 669, 573, 501, 465, 409;  $\delta_{\text{H}}$ (200 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 8.51(2H, d, J=3.03 Hz, H-1), 8.46(1H, s, H-4), 7.80(2H, d, J=8.59 Hz, H-6), 7.13(2H, d, J=3.03 Hz, H-2), 6.90(2H, d, J=8.59 Hz, H-7);  $\delta_{\text{C}}$ (101 MHz; DMSO-d<sub>6</sub>; Me<sub>4</sub>Si) 162.3(C-8), 159.5(C-3), 151.3(C-1), 149.9(C-4), 132.1(C-6), 127.6(C-5), 116.8(C-7), 116.6(C-2); m/z (ESI) 197([M-H]<sup>-</sup>, 100%), 198([M]<sup>-</sup>, 34); HRMS C<sub>12</sub>H<sub>9</sub>ON<sub>2</sub> requires 197.0720, found 197.0719.

### Synthesis of N-(4-nitrobenzyl)pyridin-4-amine **10a**.<sup>10</sup>



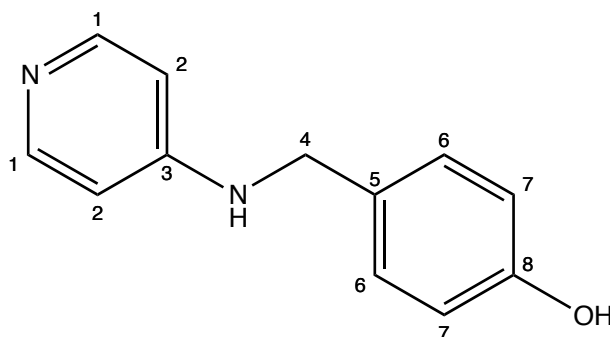
To a solution of imine **9a** (518.0 mg, 2.28 mmol) in dry MeOH (20 mL), was added powdered NaBH<sub>4</sub> (646.8 g, 17.10 mol). The mixture was kept at RT for 18 h. After completion of the reaction, water was added, and the inorganic precipitate was filtered off and washed with DCM. The organic solvent was dried (Na<sub>2</sub>SO<sub>4</sub>) and distilled off via rotary evaporation to give **10a** (118 mg, 29%) as a yellow oil:  $\nu_{\max}$ (film)/cm<sup>-1</sup> 1647(C=N), 1600, 1579, 1521(NO<sub>2</sub>), 1461, 1418, 1341(NO<sub>2</sub>), 1265, 1208, 1107;  $\delta_{\text{H}}$ (200 MHz; CD<sub>3</sub>OD; Me<sub>4</sub>Si) 8.25(2H, d, J=8.1 Hz, H-7), 8.05 (2H, d, J=5.6 Hz, H-1), 7.79 (2H, d, J=8.3 Hz, H-6), 6.66 (2H, d, J=5.6 Hz, H-2), 4.5(2H, s, H-4);  $\delta_{\text{C}}$ (101 MHz; CD<sub>3</sub>OD; Me<sub>4</sub>Si) 153.2(C-3), 148.7(C-1), 147.1(C-5), 146.6(C-8), 128.4(C-6), 123.7(C-7), 109.3(C-2), 45.4(C-4); m/z (ESI) 335(100%), 263(68), 230([M+H]<sup>+</sup>, 30).

#### Attempted synthesis of N-(4-aminobenzyl)pyridin-4-amine **10b**.<sup>11</sup>



To a stirred solution of nitro **10a** (129.1 mg, 0.56 mmol in MeOH (20 mL) at RT was added SnCl<sub>2</sub>·2H<sub>2</sub>O (676.7 mg, 3.00 mmol) in portions, following by the addition of conc HCl (0.23 mL). The reaction mixture was heated for 2h under reflux, cooled down to RT and adjusted to pH 8–9 by the addition of 1M NaOH to give red precipitates which were washed with water and the solvent was evaporated to give an orange solid which was used without further purification.

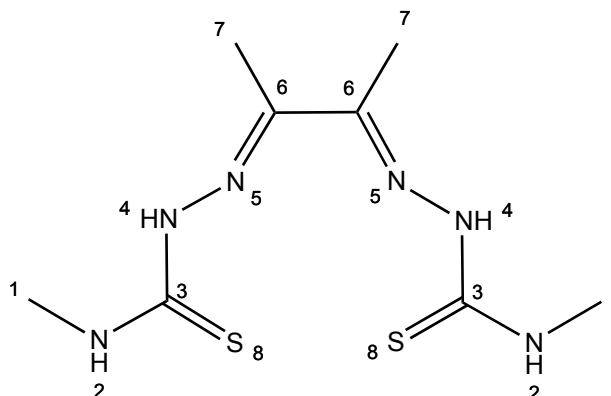
#### Synthesis of 4-((pyridin-4-ylamino)methyl)phenol **10c**.<sup>10</sup>



To a solution of imine **9b** (789 mg, 3.98 mmol) in dry MeOH (20 mL), was added powdered NaBH<sub>4</sub> (1.506 g, 39.8 mol). The mixture was kept at RT for 18h. After completion of the reaction, the solvent was removed *in vacuo* and the residue was washed with DCM. Then water was added and adjusted to pH 8–9 by the addition of 3M HCl to give white precipitates which were washed

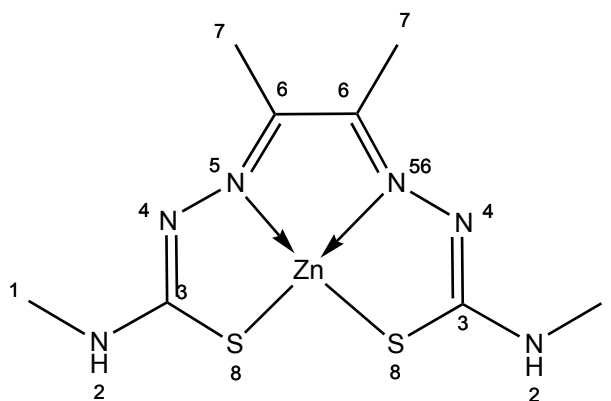
with water and filtered to afford **10c** (390 mg, 49%) as a white solid:  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3417, 2255, 2128, 1659, 1026;  $\delta_{\text{H}}(200 \text{ MHz}; \text{DMSO-d}^6; \text{Me}_4\text{Si})$  9.32(1H, br s, OH), 7.97(2H, d,  $J=5.31 \text{ Hz}$ , H-1), 7.11(2H, d,  $J=8.34 \text{ Hz}$ , H-6), 6.95(1H, t,  $J=5.56$ ,  $\text{NH}_2$ ), 6.71(2H, d,  $J=8.34 \text{ Hz}$ , H-7), 6.48(2H, d,  $J=5.31 \text{ Hz}$ , H-2), 4.16(2H, d,  $J=5.81 \text{ Hz}$ , H-4);  $\delta_{\text{C}}(101 \text{ MHz}; \text{DMSO-d}^6; \text{Me}_4\text{Si})$  157.2(C-8), 154.4(C-3), 149.8(C-1), 129.7(C-5), 129.3(C-6), 115.9(C-7), 108.2(C-2), 45.8(C-4);  $m/z$  (ESI) 201( $[\text{M}+\text{H}]^+$ , 100%), 202( $[\text{M}+2\text{H}]^+$ , 21); HRMS  $\text{C}_{12}\text{H}_{13}\text{ON}_2$  requires 201.1022, found 201.1017.

### Synthesis of Diacetyl-bis(N-4-methyl-3-thiosemicarbazone) (ATSMH<sub>2</sub>).



4-Methylthiosemicarbazide (573 mg, 5.45 mmol) was dissolved in ethanol (15 mL) and butane-2,3-dione (0.24 mL, 2.73 mmol) and conc  $\text{H}_2\text{SO}_4$  (3 drops) were added. The reaction was stirred at RT for 16h. The white precipitate was filtered, rinsed with EtOH and Et<sub>2</sub>O, then dried *in vacuo* to give ATSMH<sub>2</sub> as a white solid (344 mg, 48%);  $\nu_{\max}(\text{film})/\text{cm}^{-1}$  3442, 2250, 2125, 1662, 1053, 1024, 1005;  $\delta_{\text{H}}(200 \text{ MHz}; \text{DMSO-d}^6; \text{Me}_4\text{Si})$  10.21(2H, s, H-4), 8.37(2H, d,  $J=4.29 \text{ Hz}$ , H-2), 3.02(6H, d,  $J=4.55 \text{ Hz}$ , H-1), 2.20(6H, s, H-7);  $\delta_{\text{C}}(101 \text{ MHz}; \text{DMSO-d}^6; \text{Me}_4\text{Si})$  148.8, 32.0(C-1), 12.5(C-7);  $m/z$  (ESI) 259( $[\text{M}-\text{H}]^-$ , 100%).

### Synthesis of diacetyl-bis(N-4-methyl-3-thiosemicarbazonato) zinc(II) **13c**.



ATSMH<sub>2</sub> (344 mg, 1.32 mmol) was suspended in methanol (15 mL) and  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (300 mg, 1.37 mmol) was added. The reaction stirred at RT for 16h. The yellow precipitate was filtered, rinsed with MeOH and Et<sub>2</sub>O, then dried *in vacuo* to give **13c** as a yellow solid (115 mg, 27%);

$\nu_{\text{max}}(\text{film})/\text{cm}^{-1}$  3432, 2252, 2126, 1661, 1051, 1023;  $\delta\text{H}(200 \text{ MHz}; \text{DMSO-}d^6; \text{Me}_4\text{Si})$  7.18(2H, s, H-2), 2.82(6H, ds, H-1), 2.20(6H, s, H-7);  $\delta\text{C}(101 \text{ MHz}; \text{DMSO-}d^6; \text{Me}_4\text{Si})$  41.0, 40.7, 40.5, 40.3, 40.1, 39.9, 39.7, 14.7;  $m/z$  (ESI) 107(100%), 217(57), 323([M+H]<sup>+</sup>, 41).

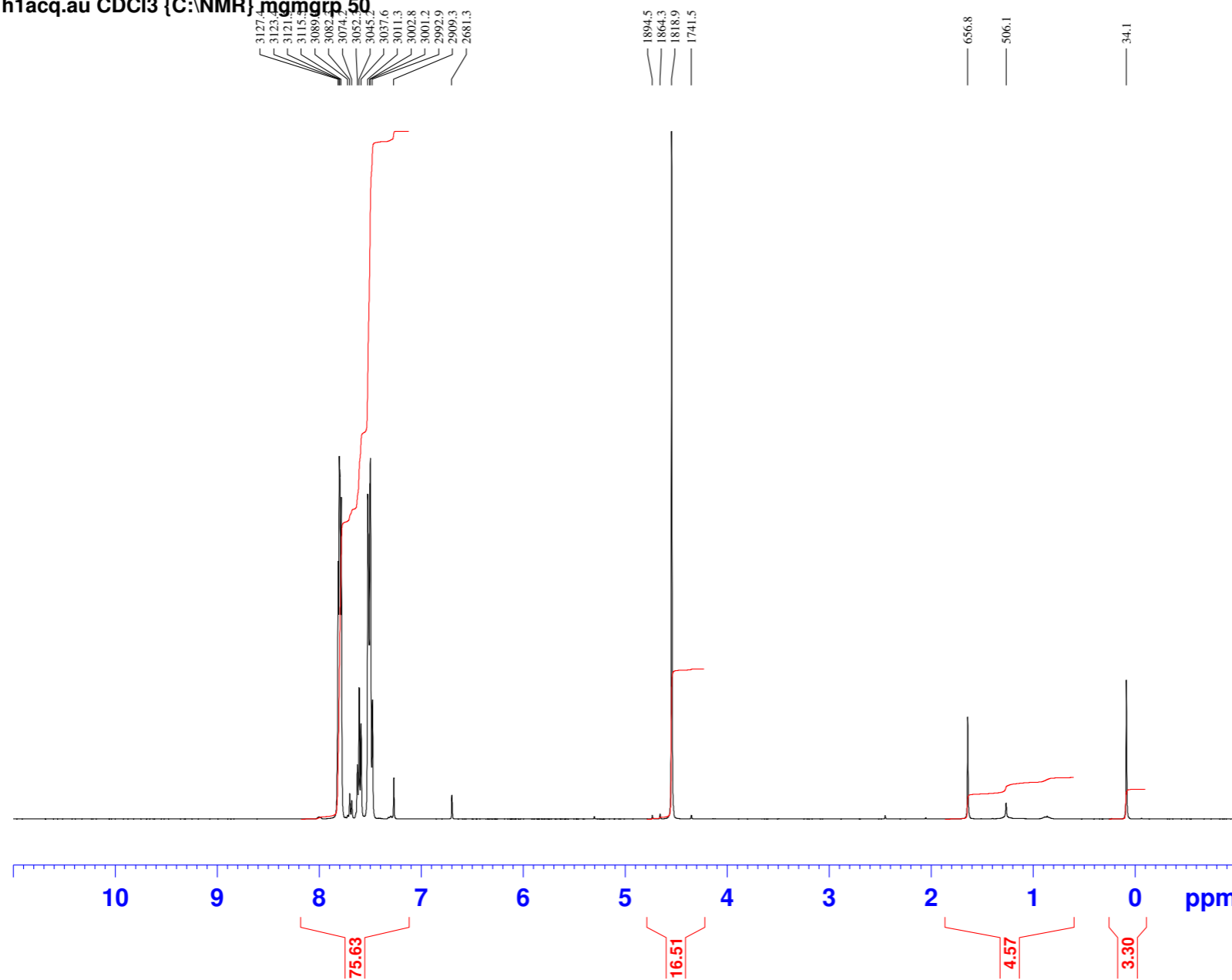
## References

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2. H. J. Dauben and L. L. McCoy, *J. Am. Chem. Soc.*, 1959, **81**, 4863-4873.
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NMR@CHEM.OX



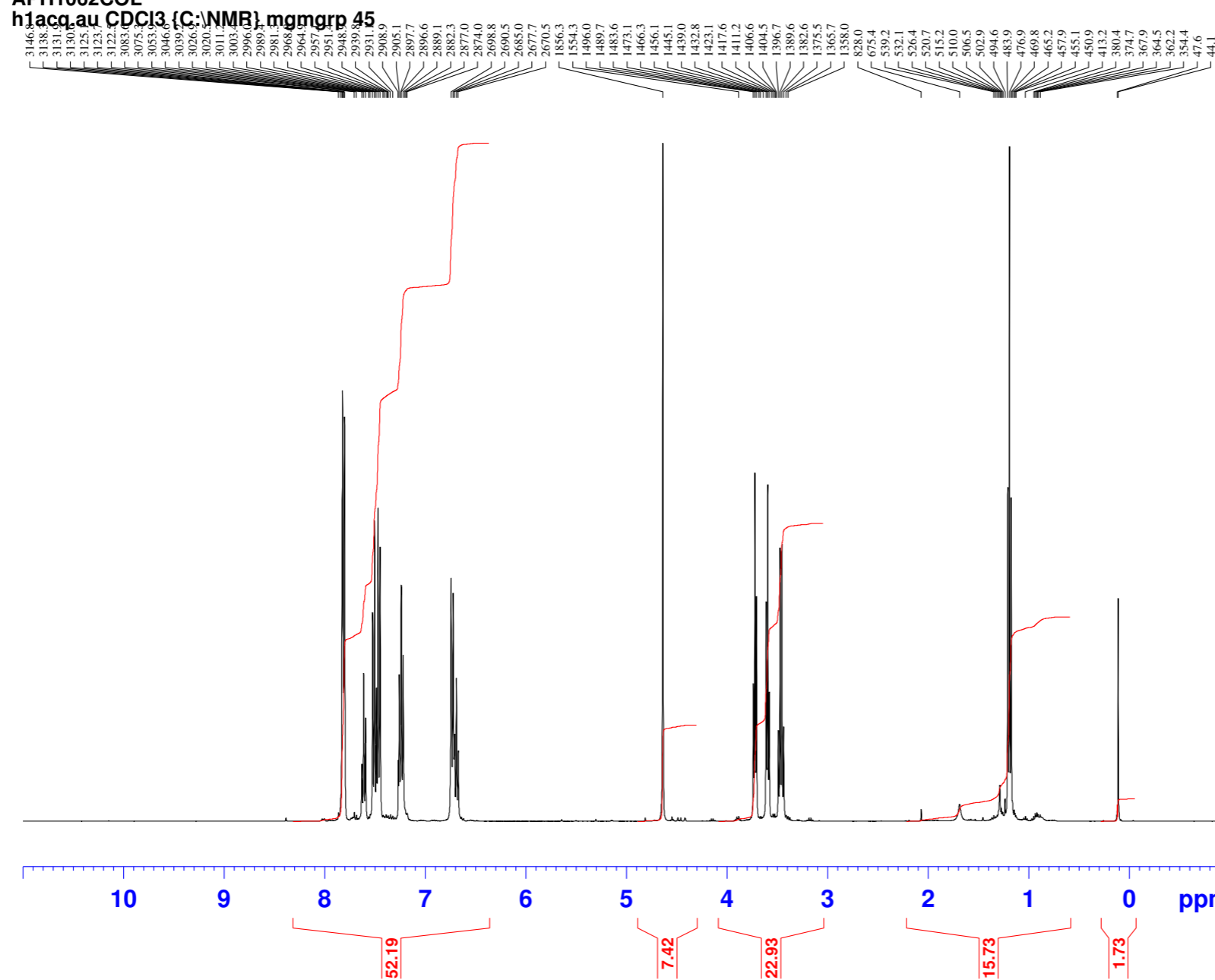
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# NMR

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Group mgm  
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NMR@CHEM.OX



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2a

# NMR

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Group mgm  
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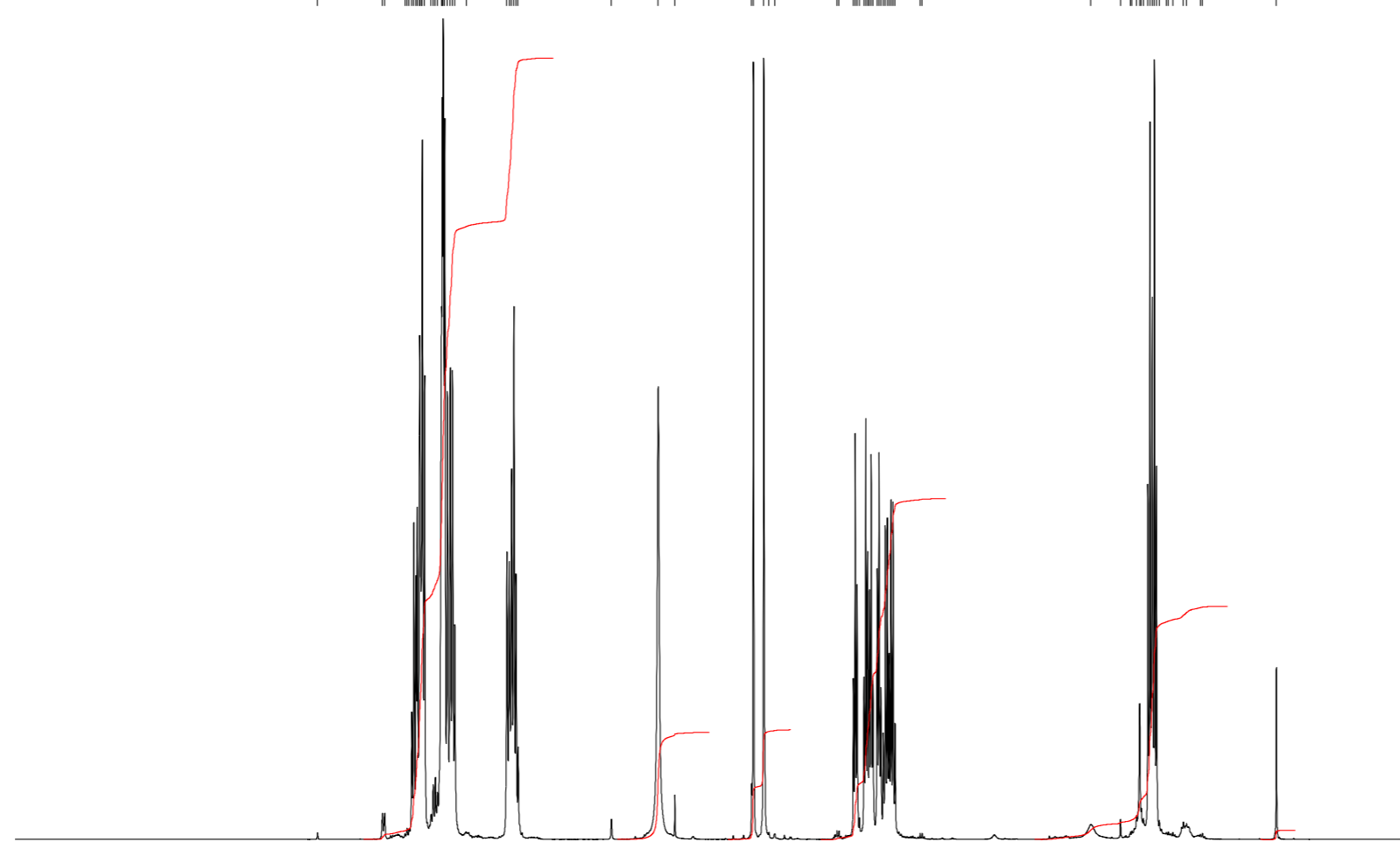
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NMR@CHEM.OX

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2b

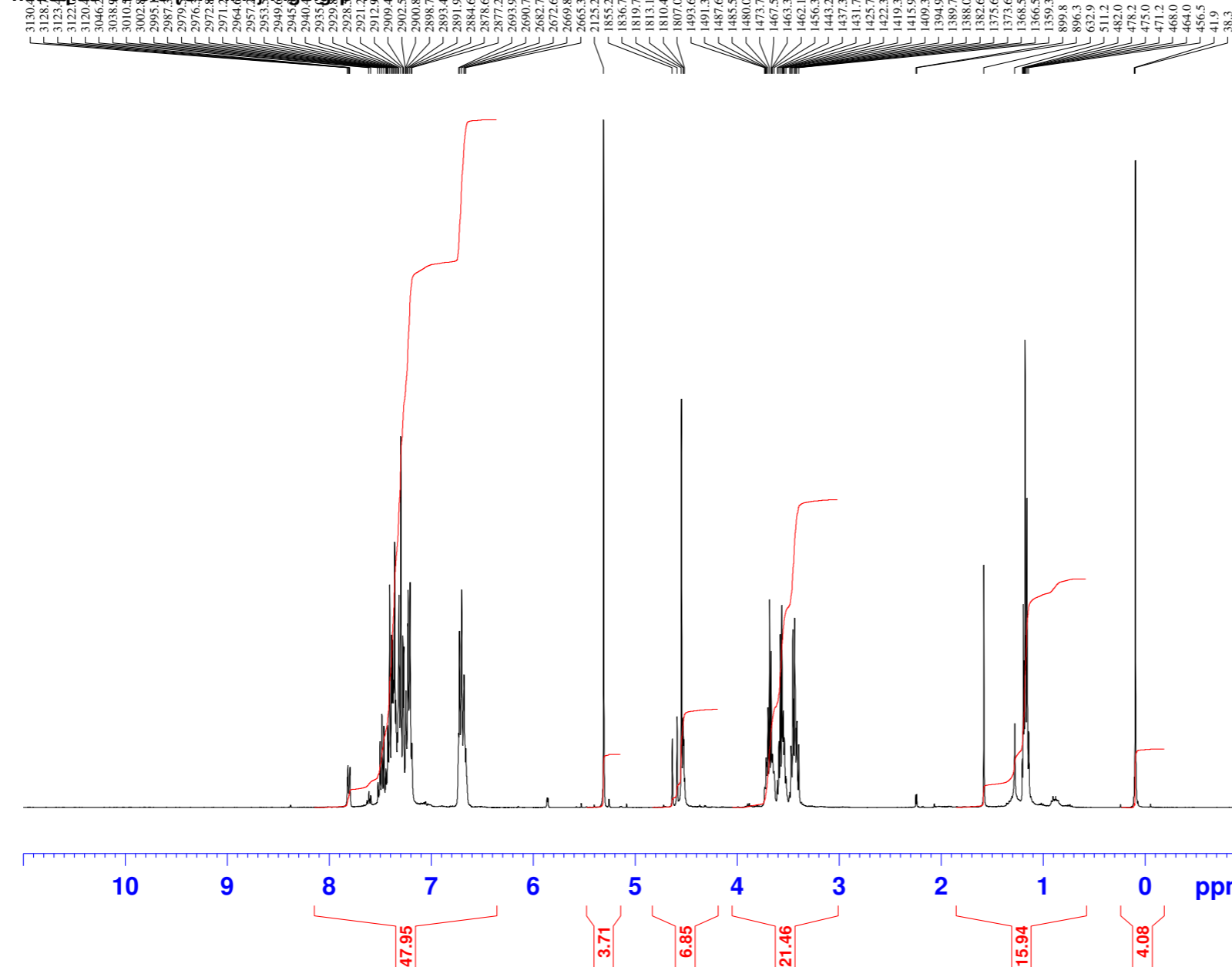


# NMR

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Group mgn  
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NMR@CHEM.OX



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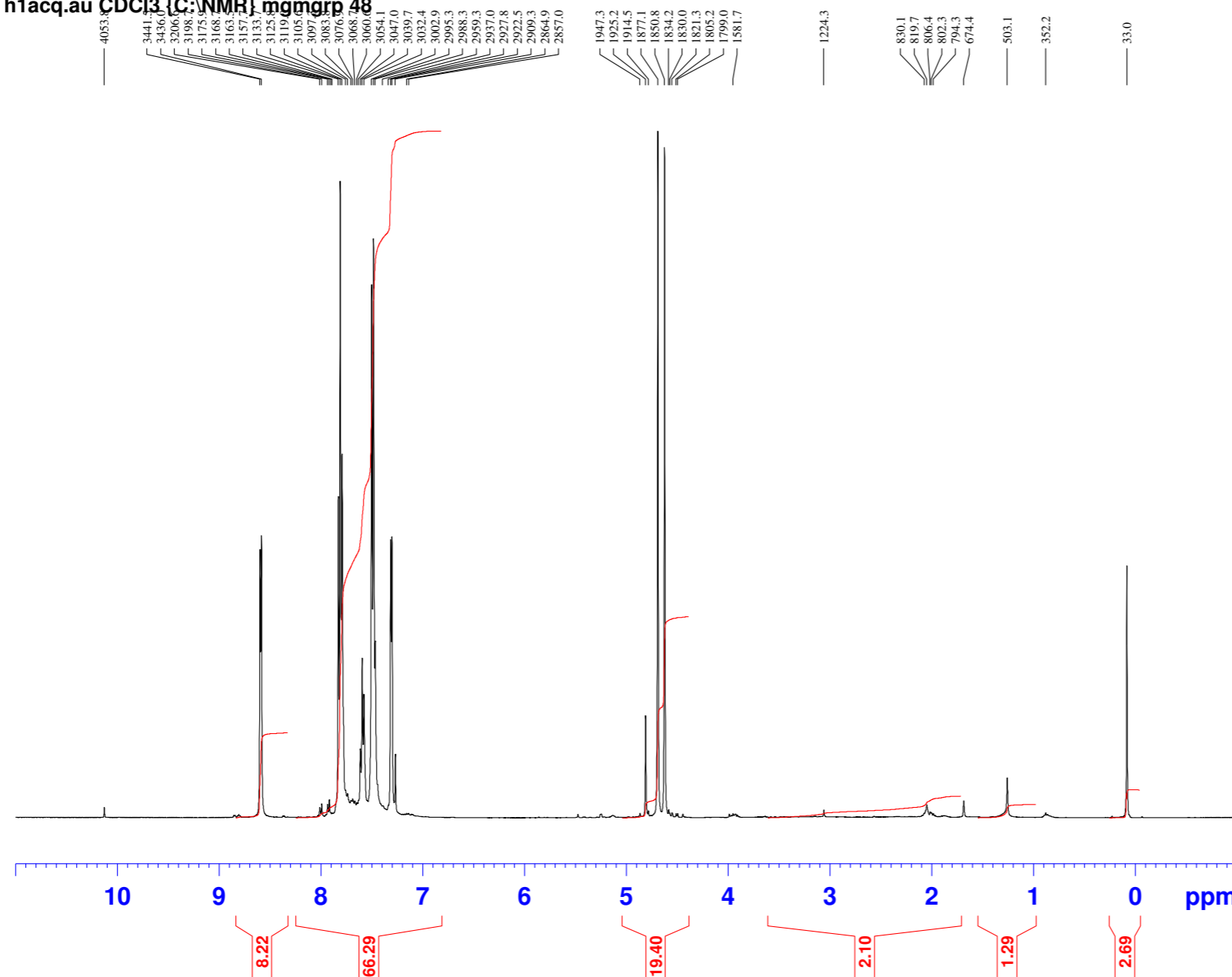
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Group mgm  
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h1acq.au

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NMR@CHEM.OX



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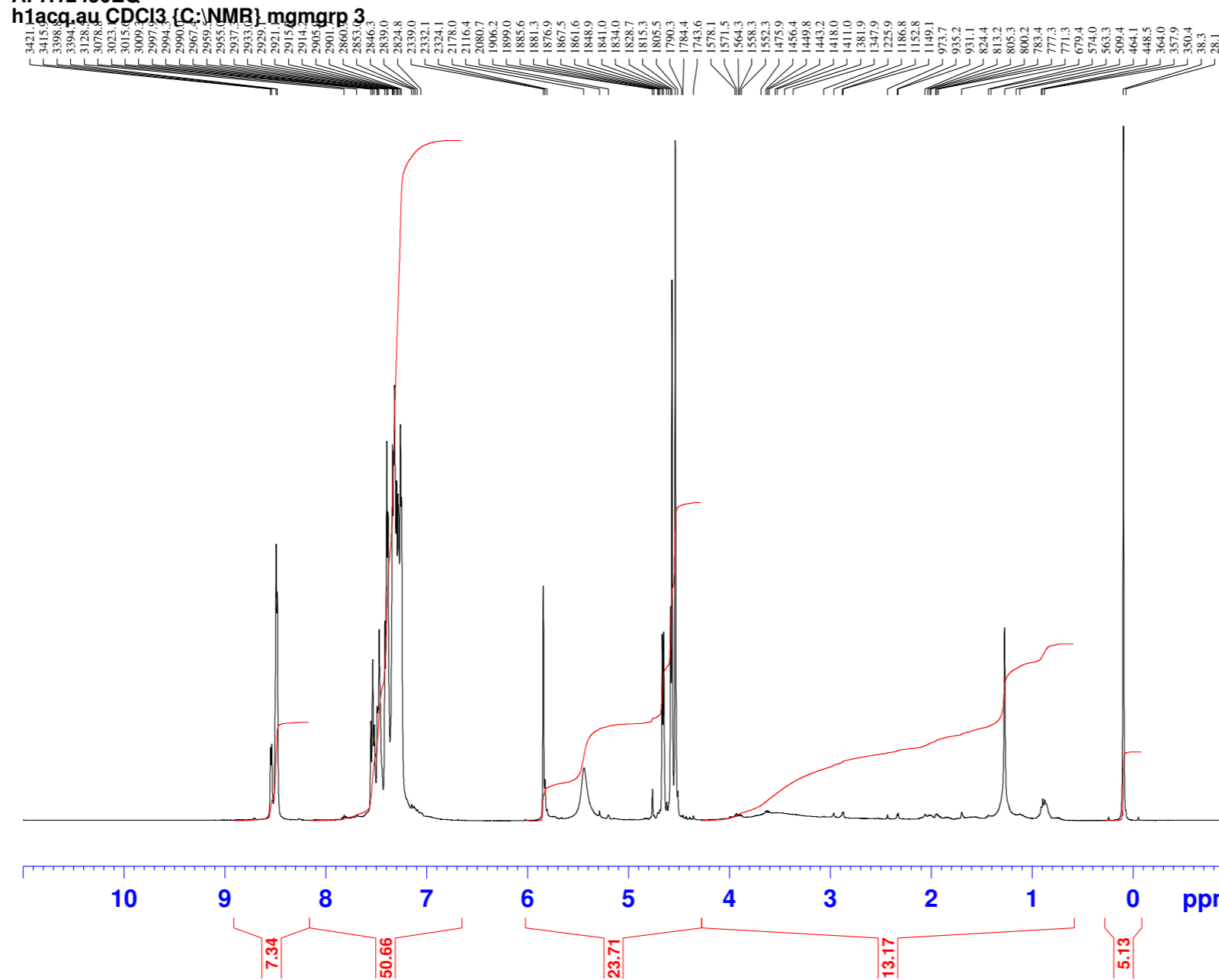
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6a

# NMR

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Group mgm  
APH12450EQ  
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NMR@CHEM.OX



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PROCNO 1  
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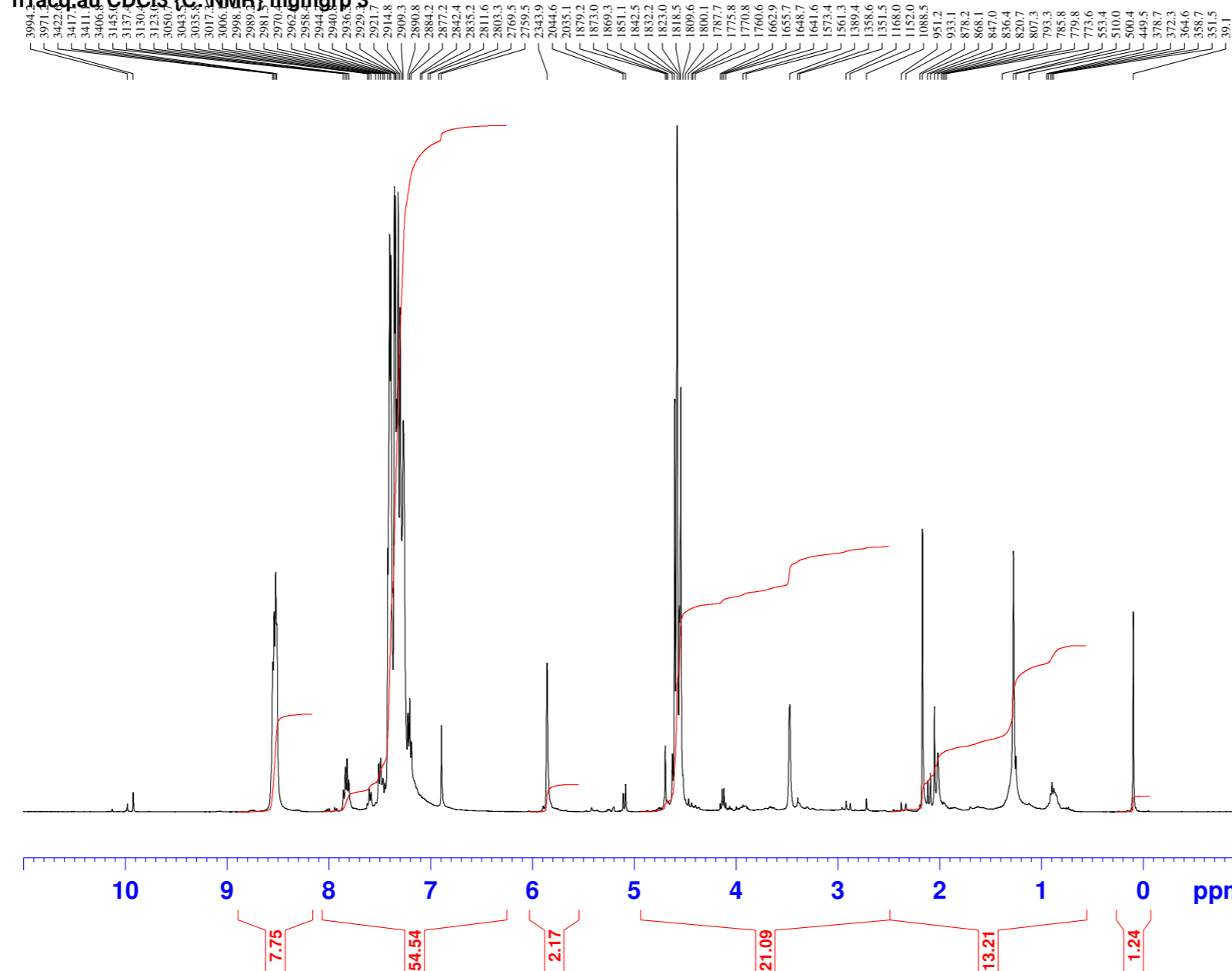
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6b

# NMR

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NMR@CHEM.OX

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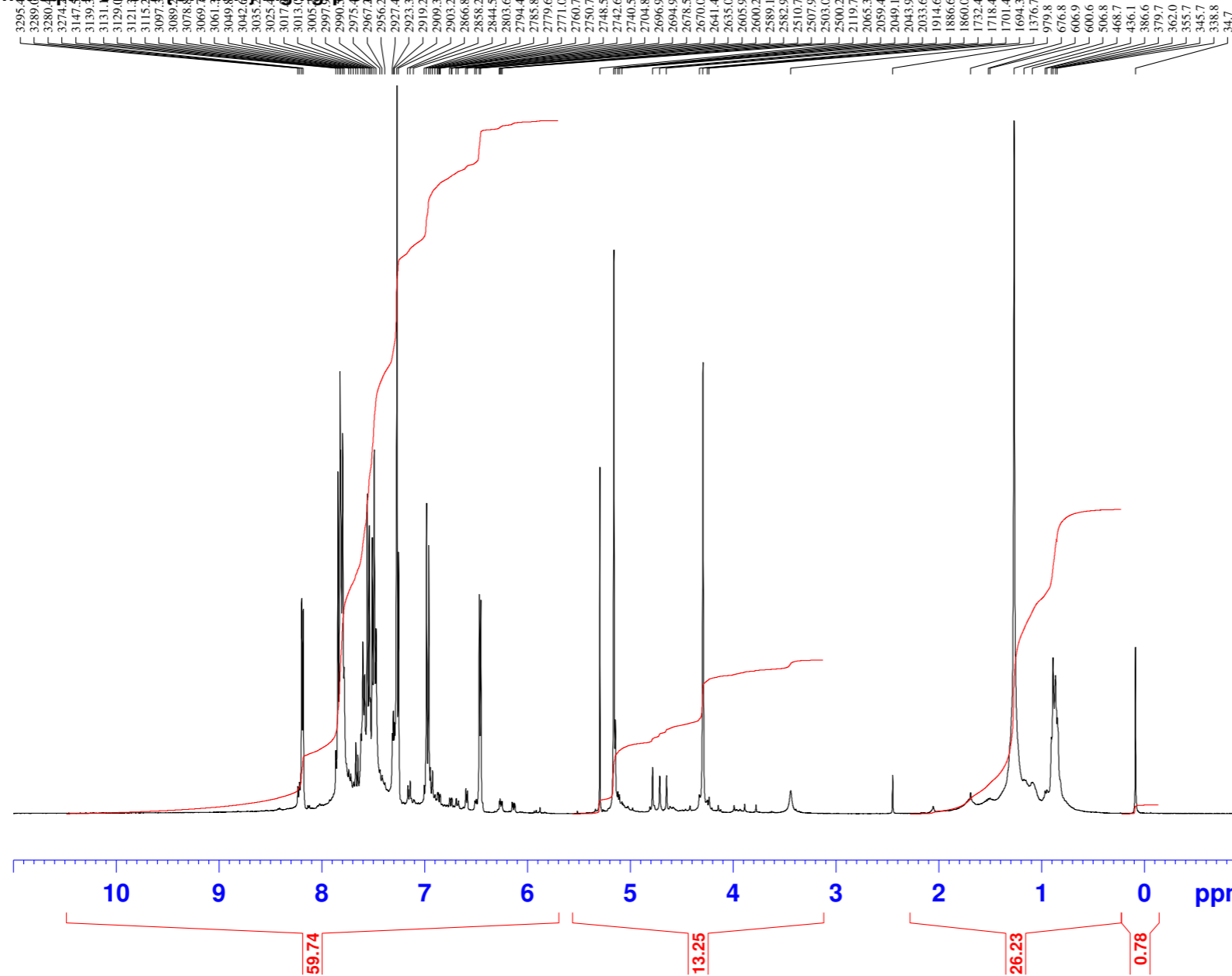
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6c

# NMR

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NMR@CHEM.OX

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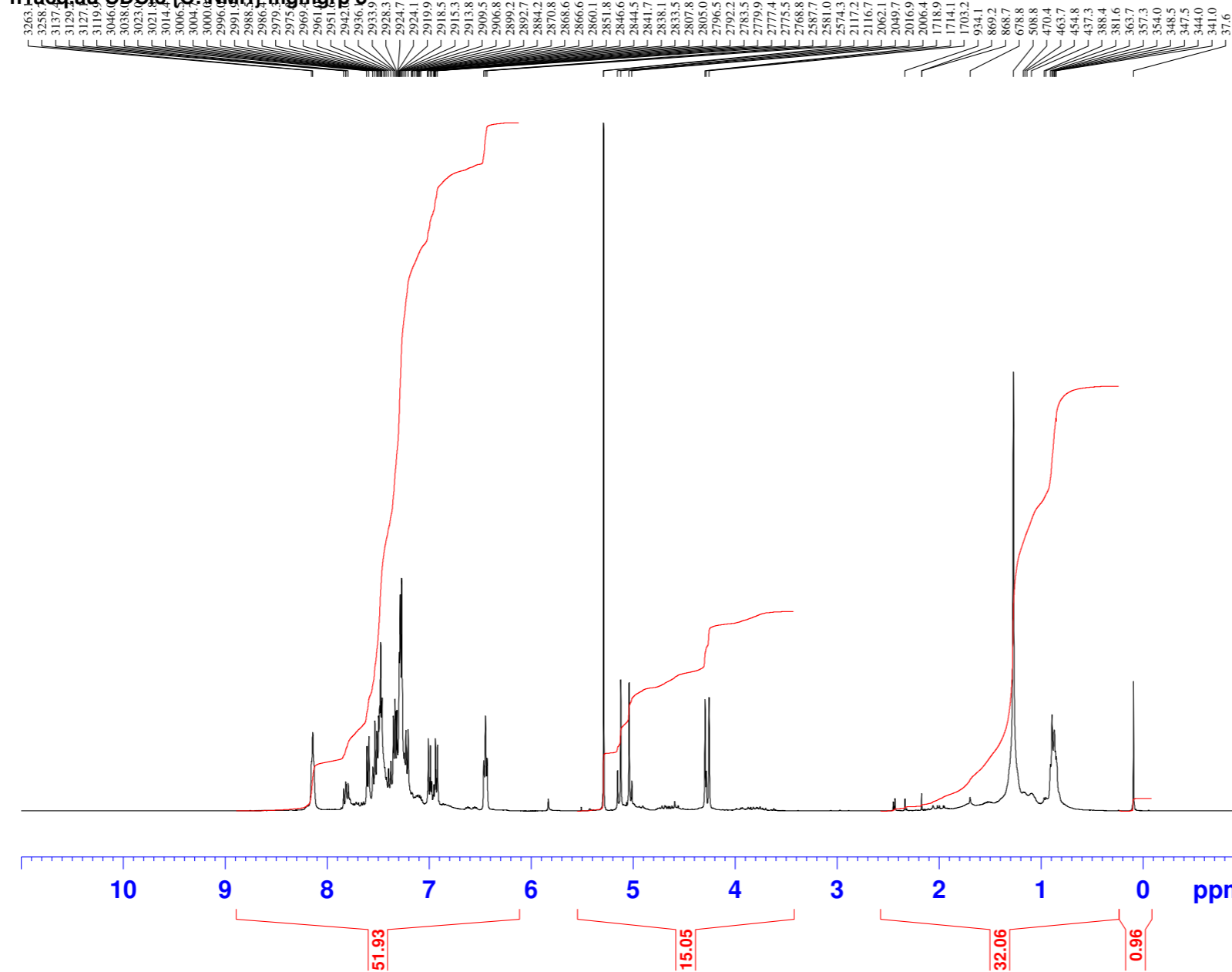
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7a

# NMR

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Chemist aaa  
Group mgm  
APH151D20

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NMR@CHEM.OX

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Group mgm  
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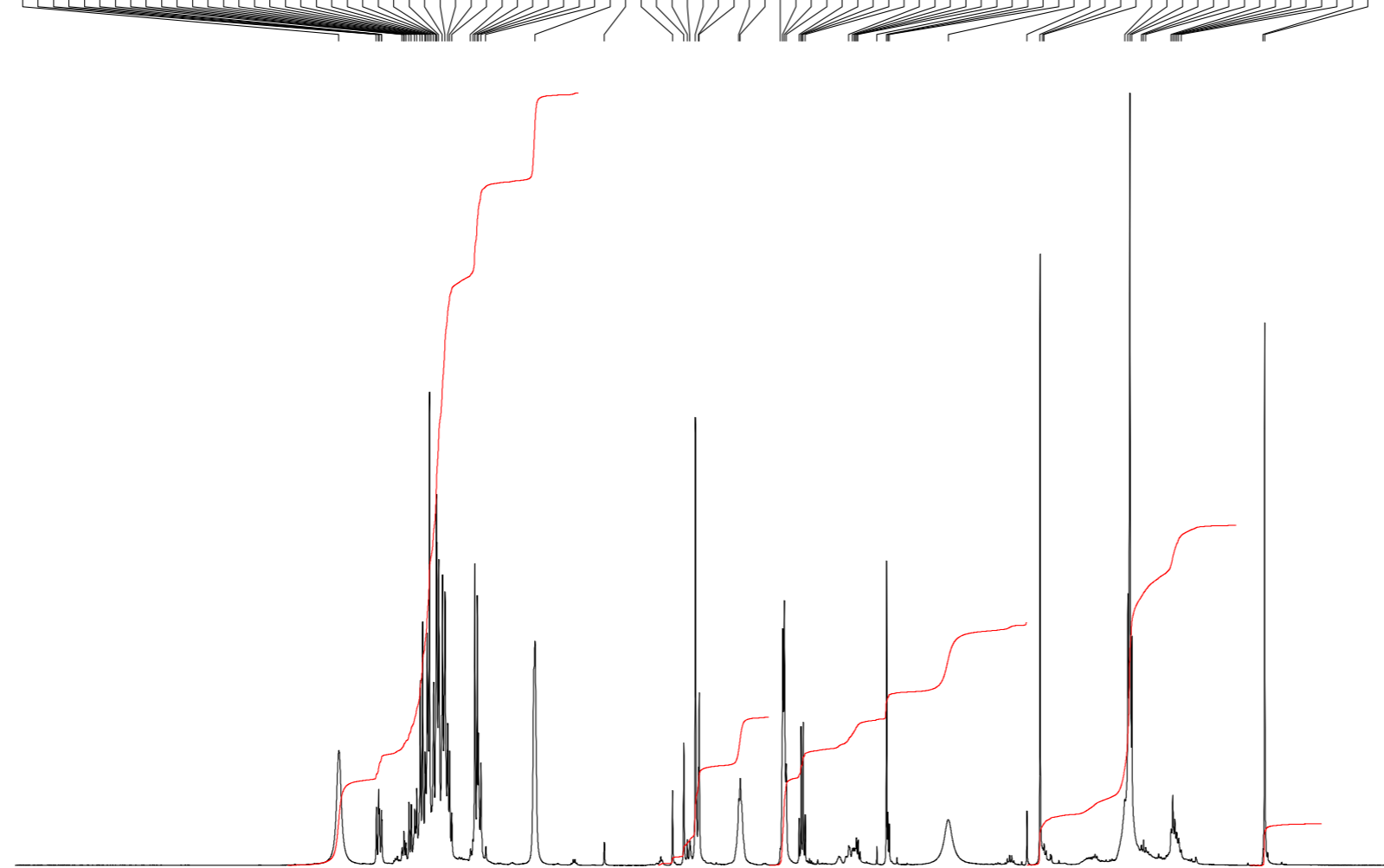
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NMR@CHEM.OX

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7c

# NMR

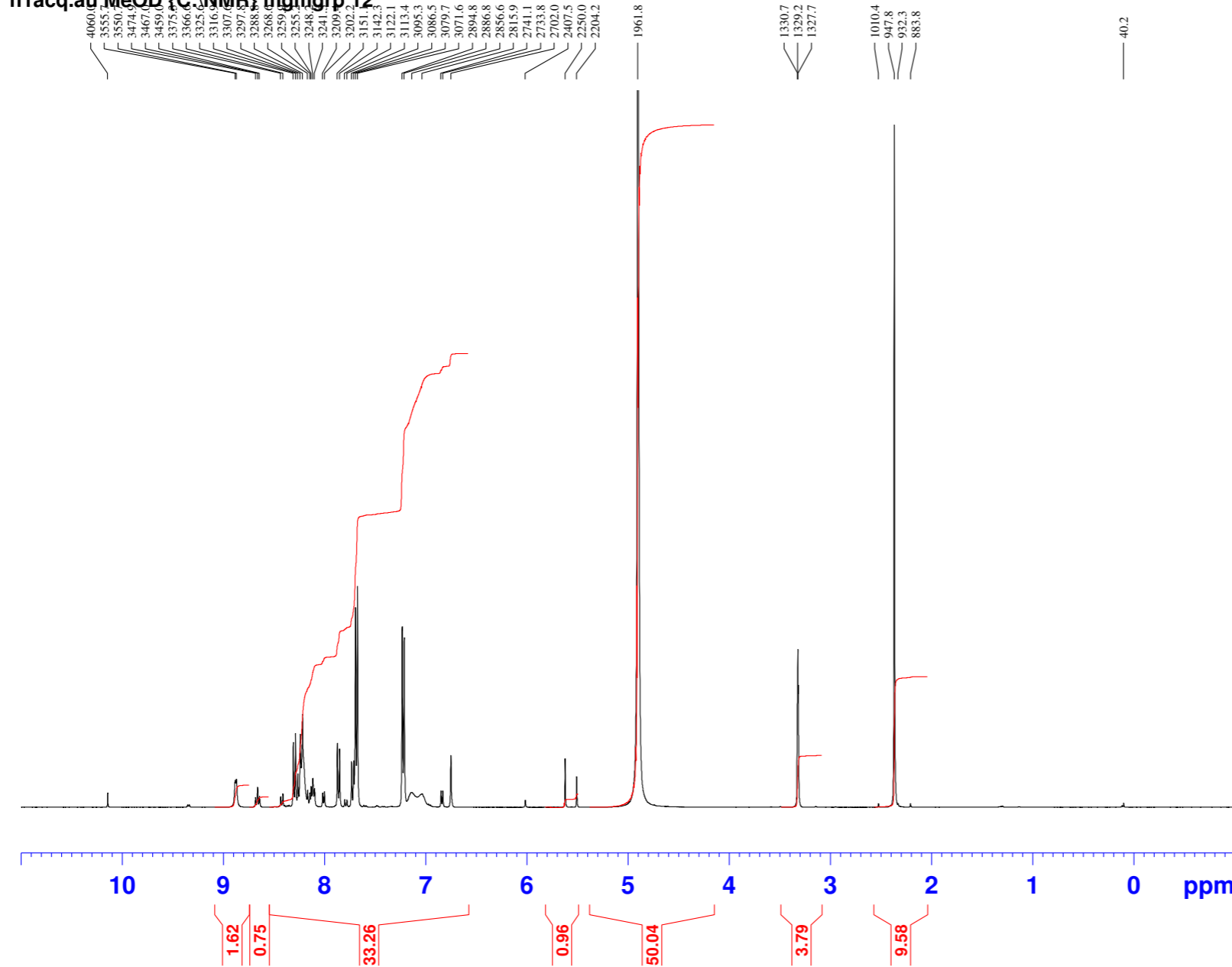
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Chemist aaa

Group mgm

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NMR@CHEM.OX

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PROCNO 1  
Date\_ 20091109  
Time 20.09  
INSTRUM av400  
PROBHD 5 mm QNP 1H/13  
PULPROG zg60  
TD 65536  
SOLVENT MeOD  
NS 16  
DS 2  
SWH 8278.146 Hz  
FIDRES 0.126314 Hz  
AQ 3.9584243 sec  
RG 90.5  
DW 60.400 usec  
DE 7.50 usec  
TE 300.0 K  
D1 1.00000000 sec

==== CHANNEL f1 =====  
NUC1 1H  
P1 9.00 usec  
PL1 0.00 dB  
SFO1 400.2024714 MHz  
SI 32768  
SF 400.2000000 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

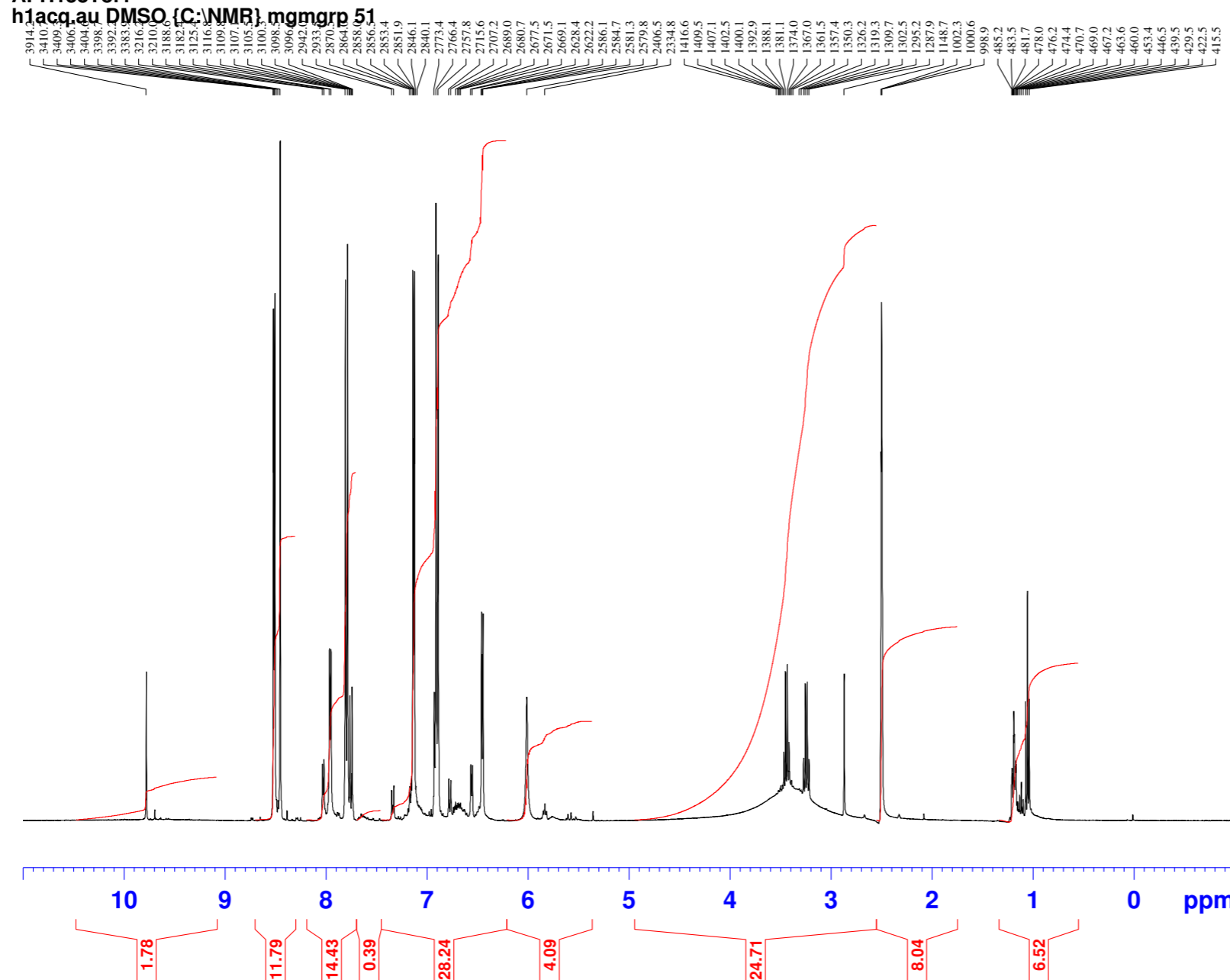
9a



# NMR

Instrument DQX400  
Chemist aaa  
Group mgm  
APH138Tol4  
h1acq au DMSO (C-NMR) mgmgrp 51

NMR@CHEM.OX



```
NAME      Jul09-2010-51
EXPNO     1
PROCNO    1
Date_     20100709
Time      23.15
INSTRUM   av400
PROBHD    5 mm QNP 1H/13
PULPROG   zg60
TD        65536
SOLVENT   DMSO
NS        16
DS        2
SWH       8278.146 Hz
FIDRES    0.126314 Hz
AQ        3.9584243 sec
RG        161.3
DW        60.400 usec
DE        7.50 usec
TE        300.0 K
D1        1.00000000 sec
```

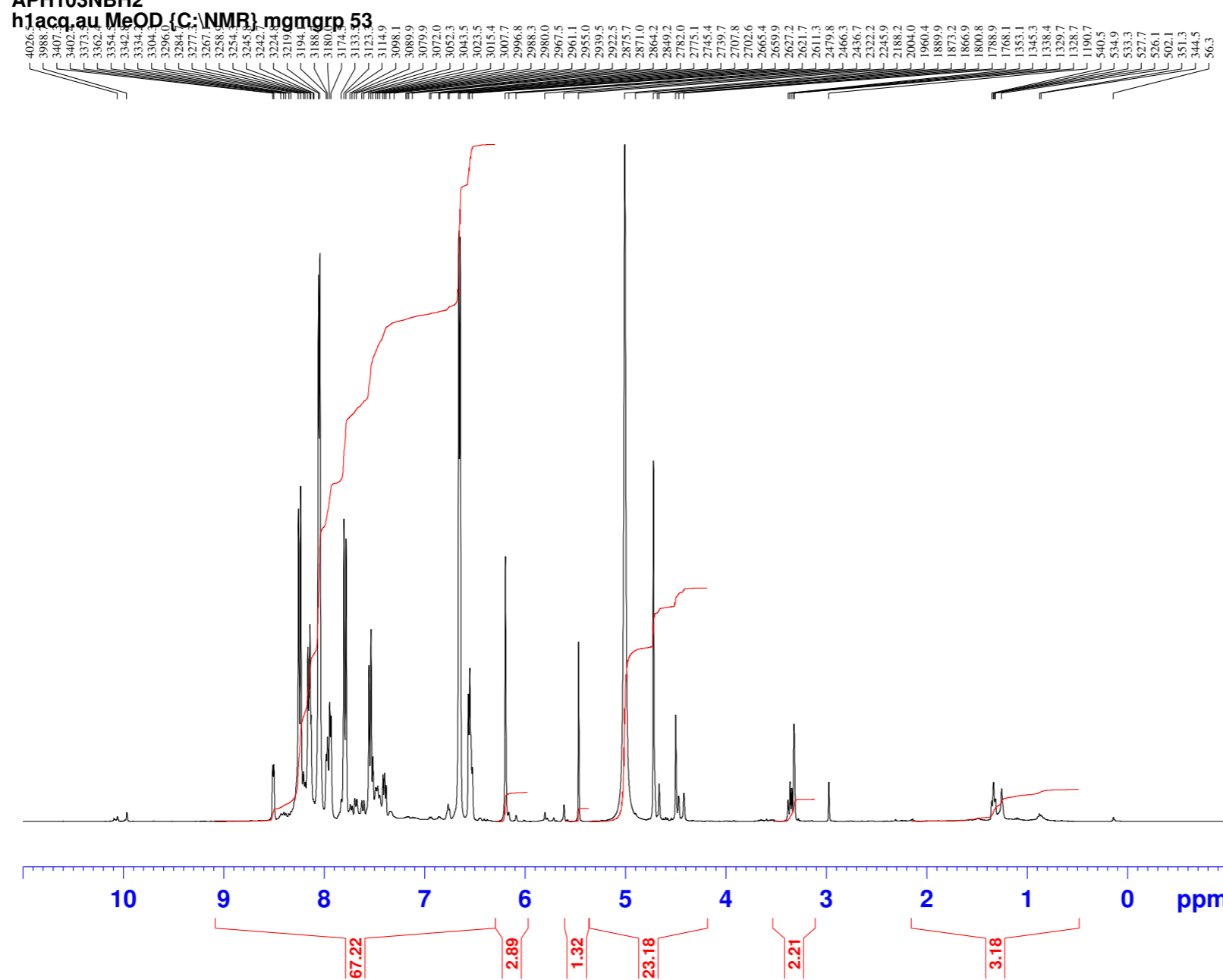
```
===== CHANNEL f1 =====
NUC1      1H
P1        9.00 usec
PL1       0.00 dB
SFO1     400.2024714 MHz
SI        32768
SF        400.2000000 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
```

9b

# NMR

Instrument DQX400  
Chemist aaa  
Group mgm  
APH103NBH2  
h1acq au MeOD (C:\NMR) mgmgrp 53

NMR@CHEM.OX



```
NAME      Apr14-2010-53
EXPNO     1
PROCNO    1
Date_     20100414
Time      21.03
INSTRUM   av400
PROBHD    5 mm QNP 1H/13
PULPROG   zg60
TD         65536
SOLVENT   MeOD
NS         16
DS         2
SWH       8278.146 Hz
FIDRES    0.126314 Hz
AQ         3.9584243 sec
RG         32
DW         60.400 usec
DE         7.50 usec
TE         300.0 K
D1         1.00000000 sec
```

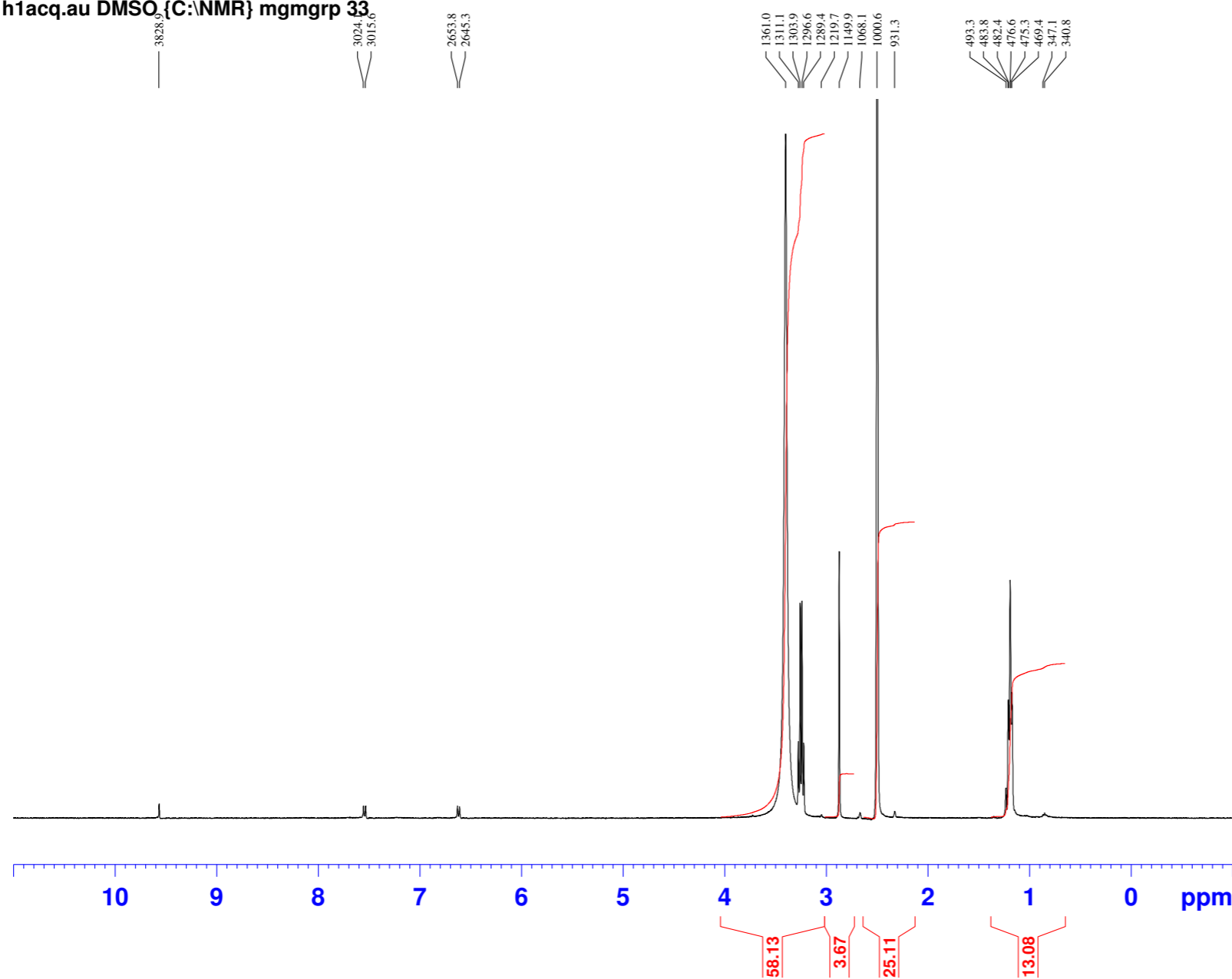
```
===== CHANNEL f1 =====
NUC1      1H
P1         9.00 usec
PL1        0.00 dB
SFO1      400.2024714 MHz
SI         32768
SF         400.2000000 MHz
WDW        EM
SSB         0
LB         0.30 Hz
GB          0
PC         1.00
```

10a

# NMR

Instrument DQX400  
Chemist aaa  
Group mgm  
APH1082  
h1acq.au DMSO {C:NMR} mgmgrp 33

NMR@CHEM.OX



```
NAME      Apr23-2010-33
EXPNO     1
PROCNO    1
Date_     20100424
Time      2.15
INSTRUM   av400
PROBHD    5 mm QNP 1H/13
PULPROG   zg60
TD         65536
SOLVENT   DMSO
NS         16
DS         2
SWH       8278.146 Hz
FIDRES    0.126314 Hz
AQ        3.9584243 sec
RG         362
DW        60.400 usec
DE         7.50 usec
TE         300.0 K
D1        1.00000000 sec
```

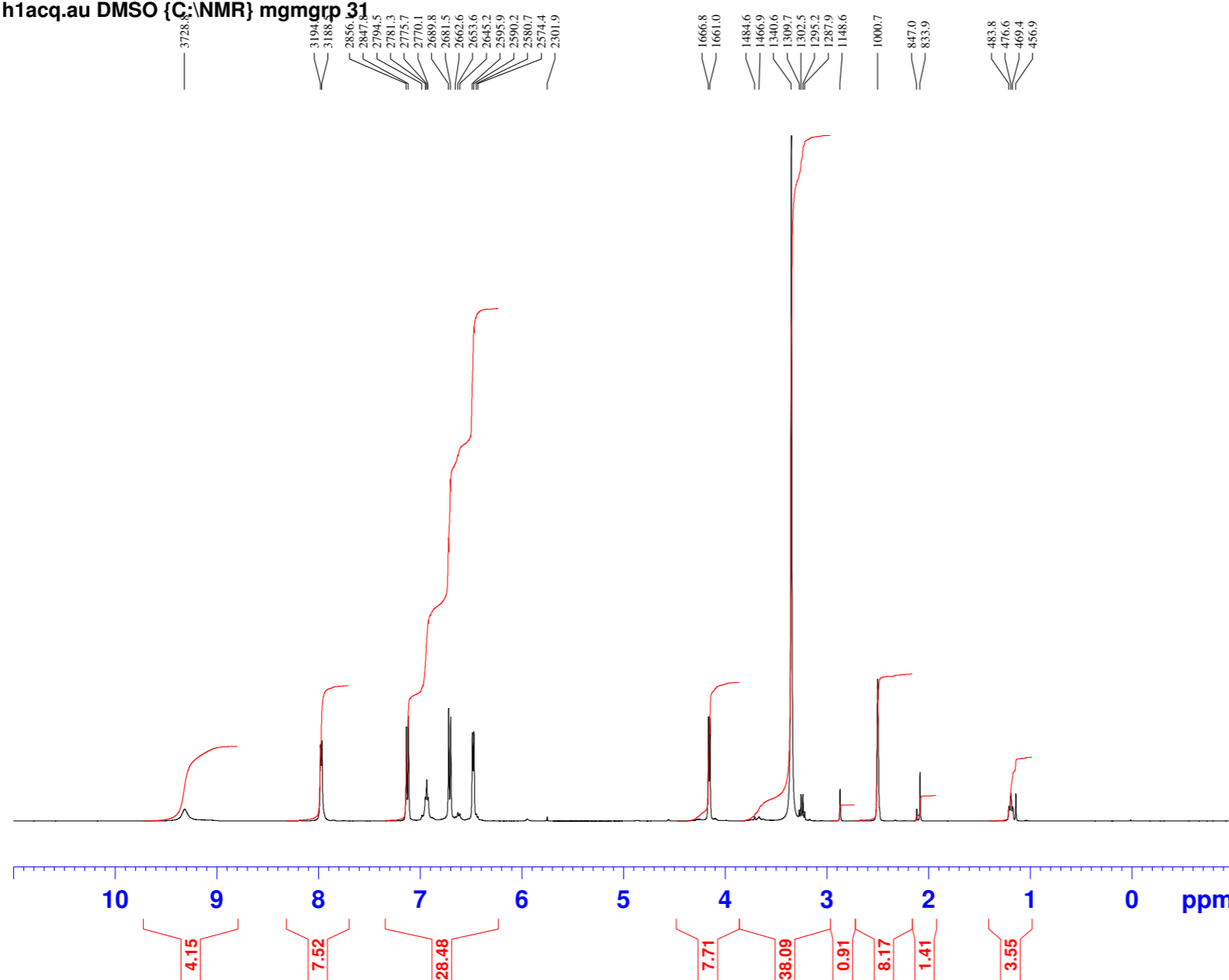
```
===== CHANNEL f1 =====
NUC1      1H
P1        9.00 usec
PL1       0.00 dB
SFO1     400.2024714 MHz
SI        32768
SF        400.2000000 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB         0
PC        1.00
```

10b

# NMR

Instrument DQX400  
Chemist aaa  
Group mgm  
APH1413  
h1acq.au DMSO {C:\NMR} mgmgrp 31

NMR@CHEM.OX



NAME Jul19-2010-31  
EXPNO 1  
PROCNO 1  
Date\_ 20100719  
Time 22.51  
INSTRUM av400  
PROBHD 5 mm QNP 1H/13  
PULPROG zg60  
TD 65536  
SOLVENT DMSO  
NS 16  
DS 2  
SWH 8278.146 Hz  
FIDRES 0.126314 Hz  
AQ 3.9584243 sec  
RG 181  
DW 60.400 usec  
DE 7.50 usec  
TE 300.0 K  
D1 1.00000000 sec

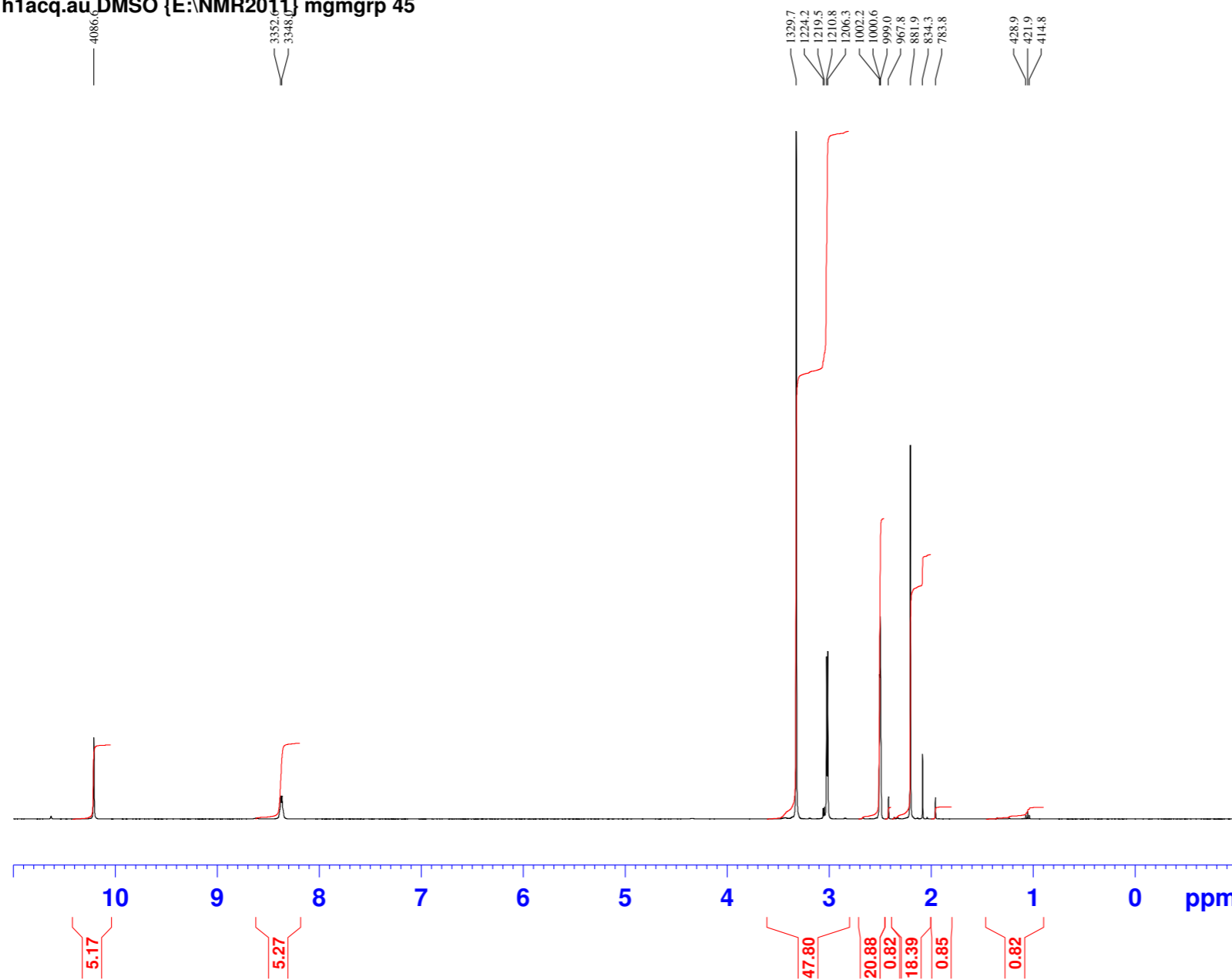
==== CHANNEL f1 =====  
NUC1 1H  
P1 9.00 usec  
PL1 0.00 dB  
SFO1 400.2024714 MHz  
SI 32768  
SF 400.2000000 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

10c

# NMR

Instrument DQX400  
Chemist aaa  
Group mgm  
ATSM2  
h1acq.au\_DMSO {E:\NMR2011} mgmgrp 45

NMR@CHEM.OX



NAME May16-2011-45  
EXPNO 1  
PROCNO 1  
Date\_ 20110516  
Time 23.58  
INSTRUM av400  
PROBHD 5 mm QNP 1H/13  
PULPROG zg60  
TD 65536  
SOLVENT DMSO  
NS 16  
DS 2  
SWH 8278.146 Hz  
FIDRES 0.126314 Hz  
AQ 3.9584243 sec  
RG 362  
DW 60.400 usec  
DE 7.50 usec  
TE 300.0 K  
D1 1.00000000 sec

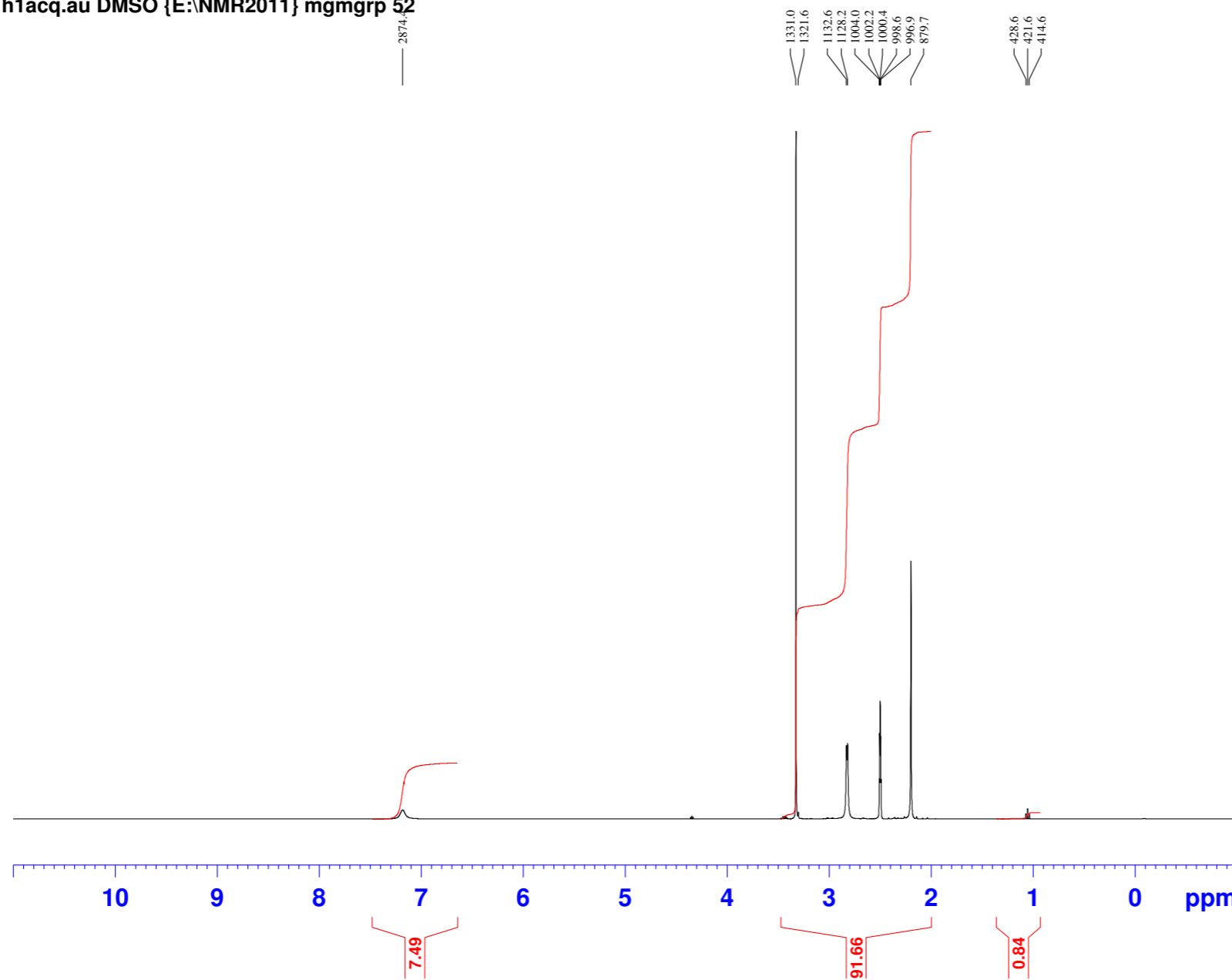
==== CHANNEL f1 =====  
NUC1 1H  
P1 9.00 usec  
PL1 0.00 dB  
SFO1 400.2024714 MHz  
SI 32768  
SF 400.2000000 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

## ATSMH<sub>2</sub>

# NMR

Instrument DQX400  
Chemist aaa  
Group mgm  
ZnATSM3  
h1acq.au DMSO {E:\NMR2011} mgmgrp 52

NMR@CHEM.OX

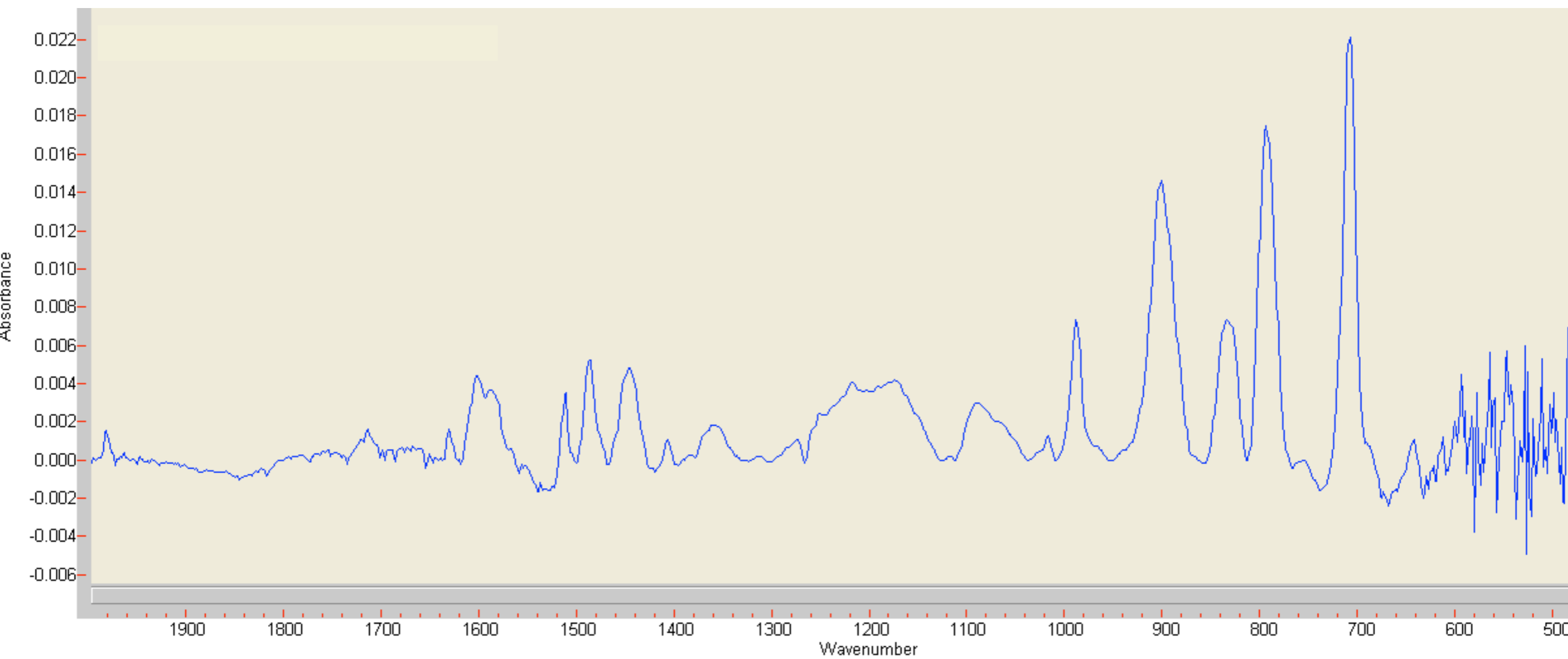


```
NAME May20-2011-52
EXPNO 1
PROCNO 1
Date_ 20110521
Time 14.44
INSTRUM av400
PROBHD 5 mm QNP 1H/13
PULPROG zg60
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 322.5
DW 60.400 usec
DE 7.50 usec
TE 300.0 K
D1 1.00000000 sec
```

```
===== CHANNEL f1 =====
NUC1 1H
P1 9.00 usec
PL1 0.00 dB
SFO1 400.2024714 MHz
SI 32768
SF 400.2000000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
```

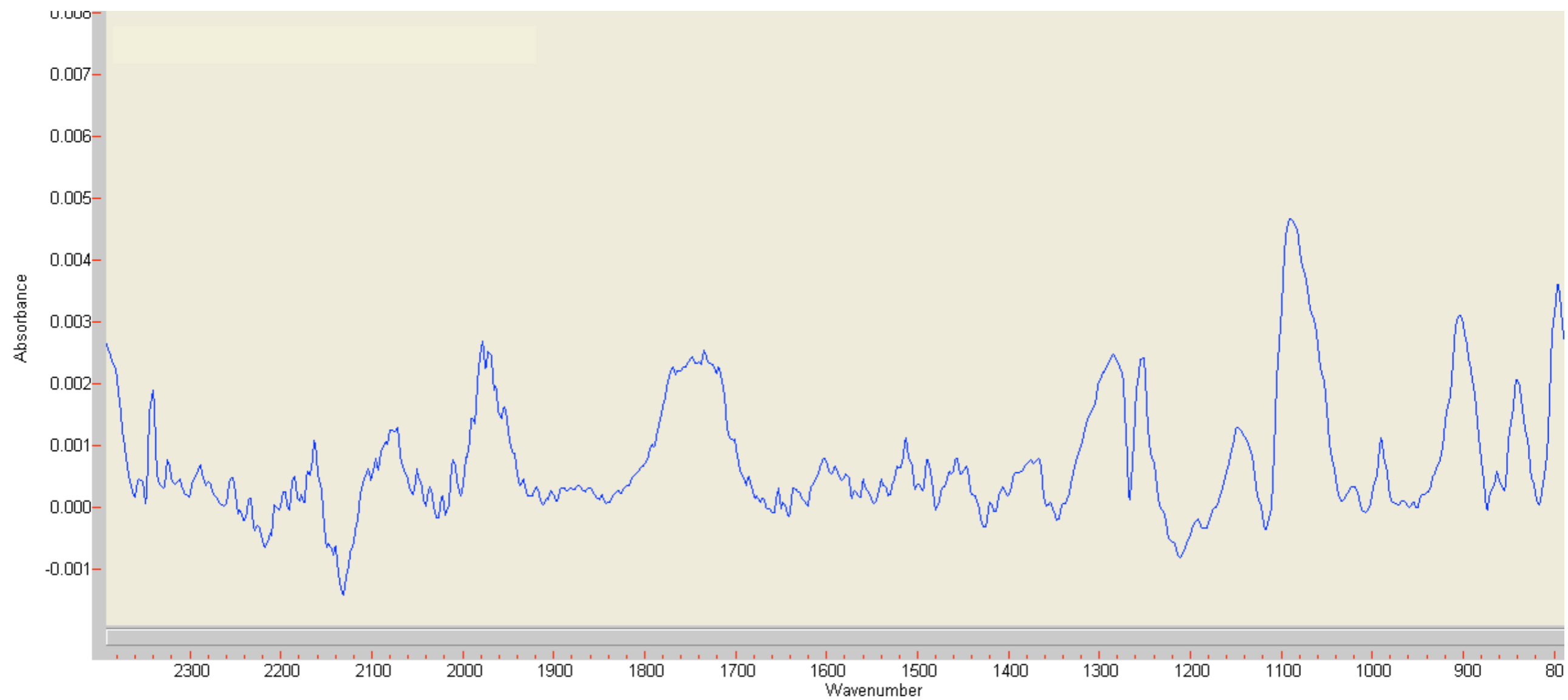
## 13C

# ATR-IR



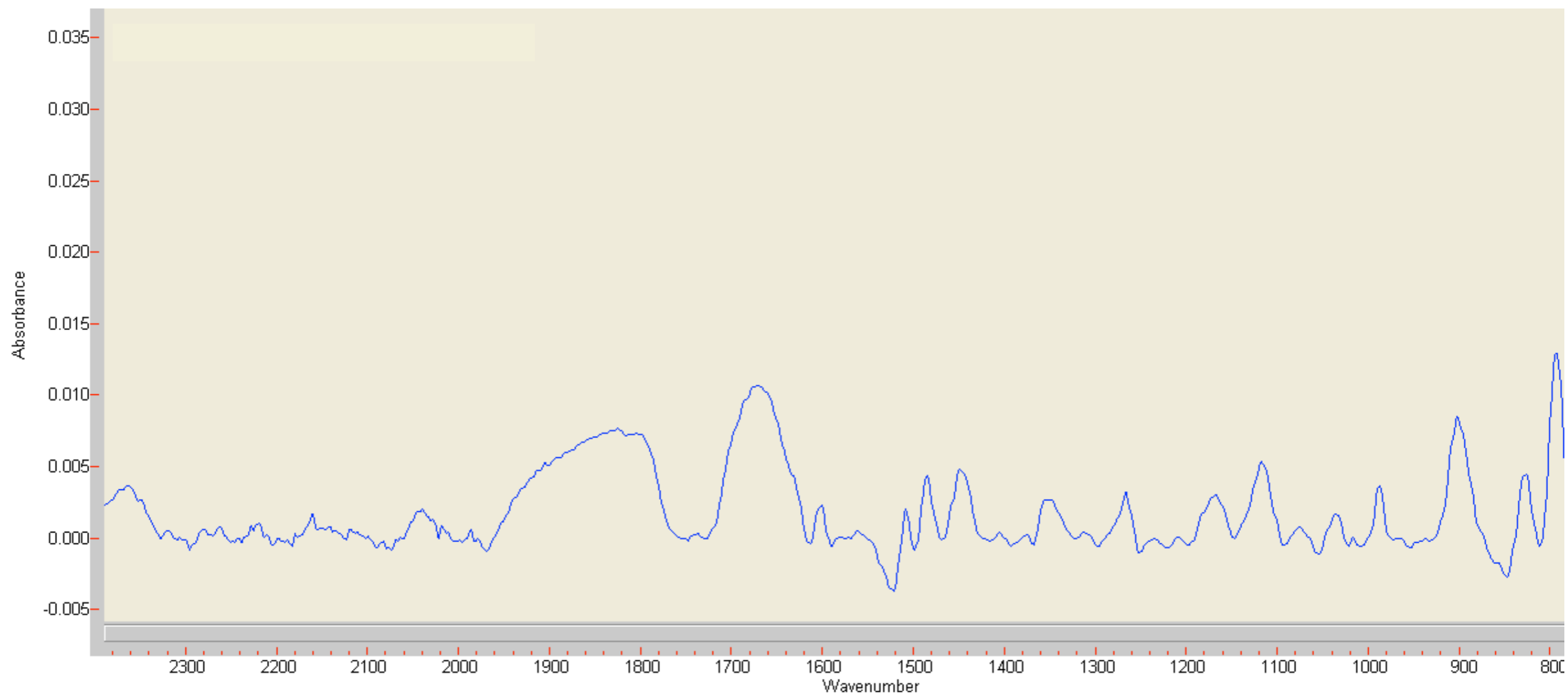
# PS XAD

# ATR-IR



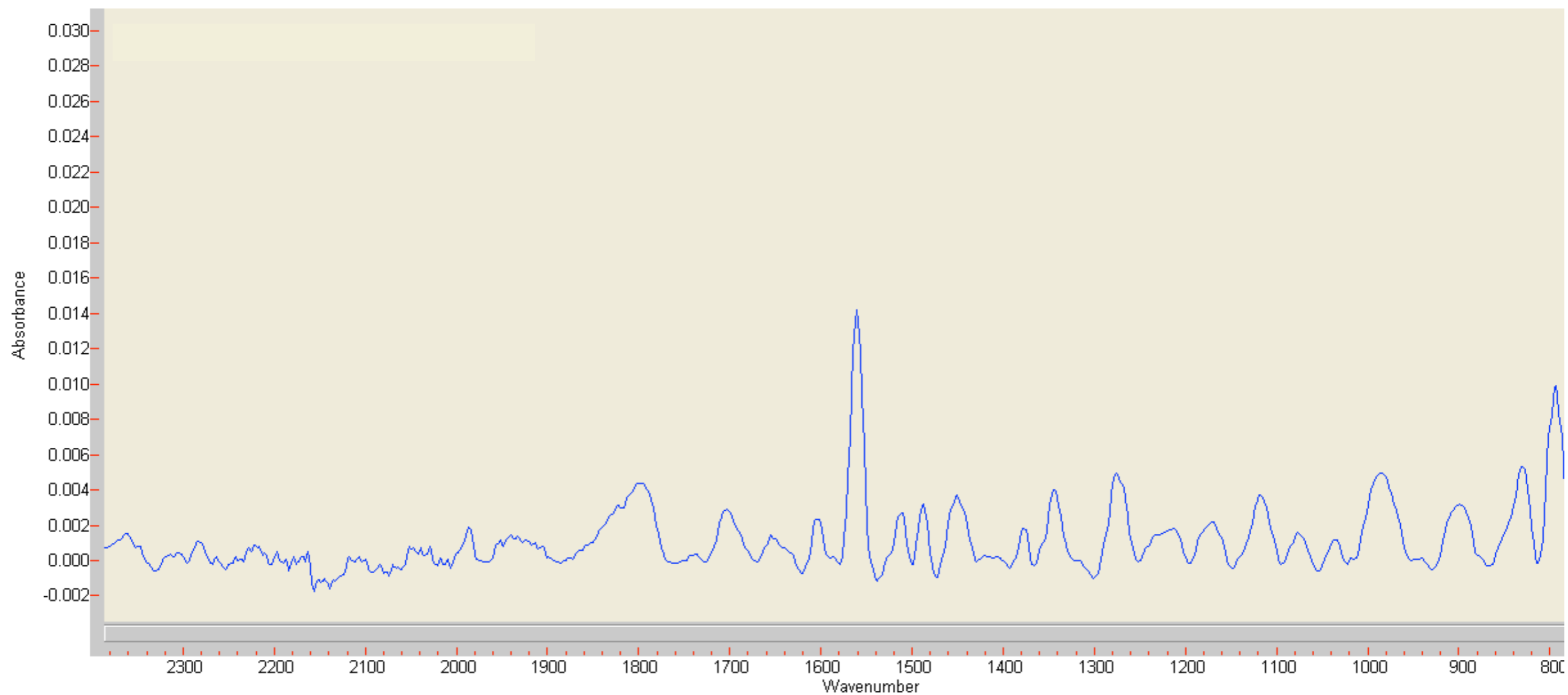


# ATR-IR



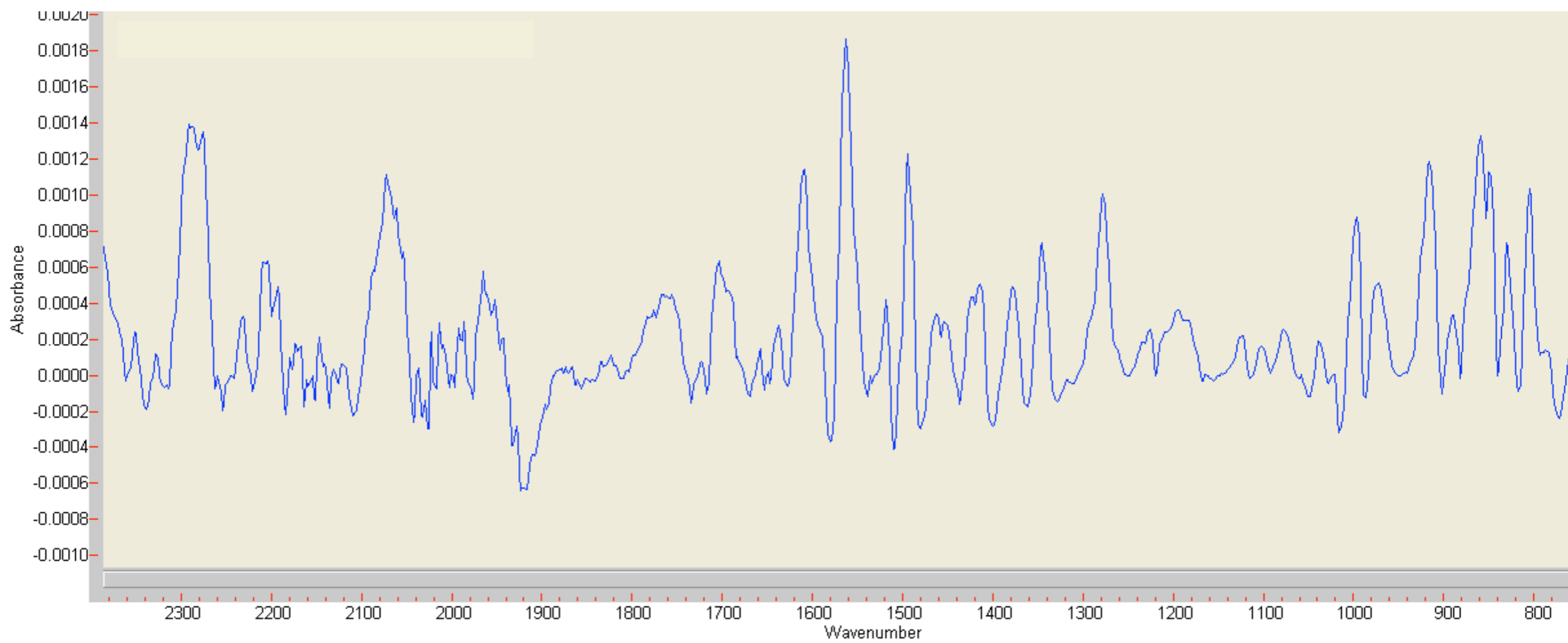
5a

# ATR-IR



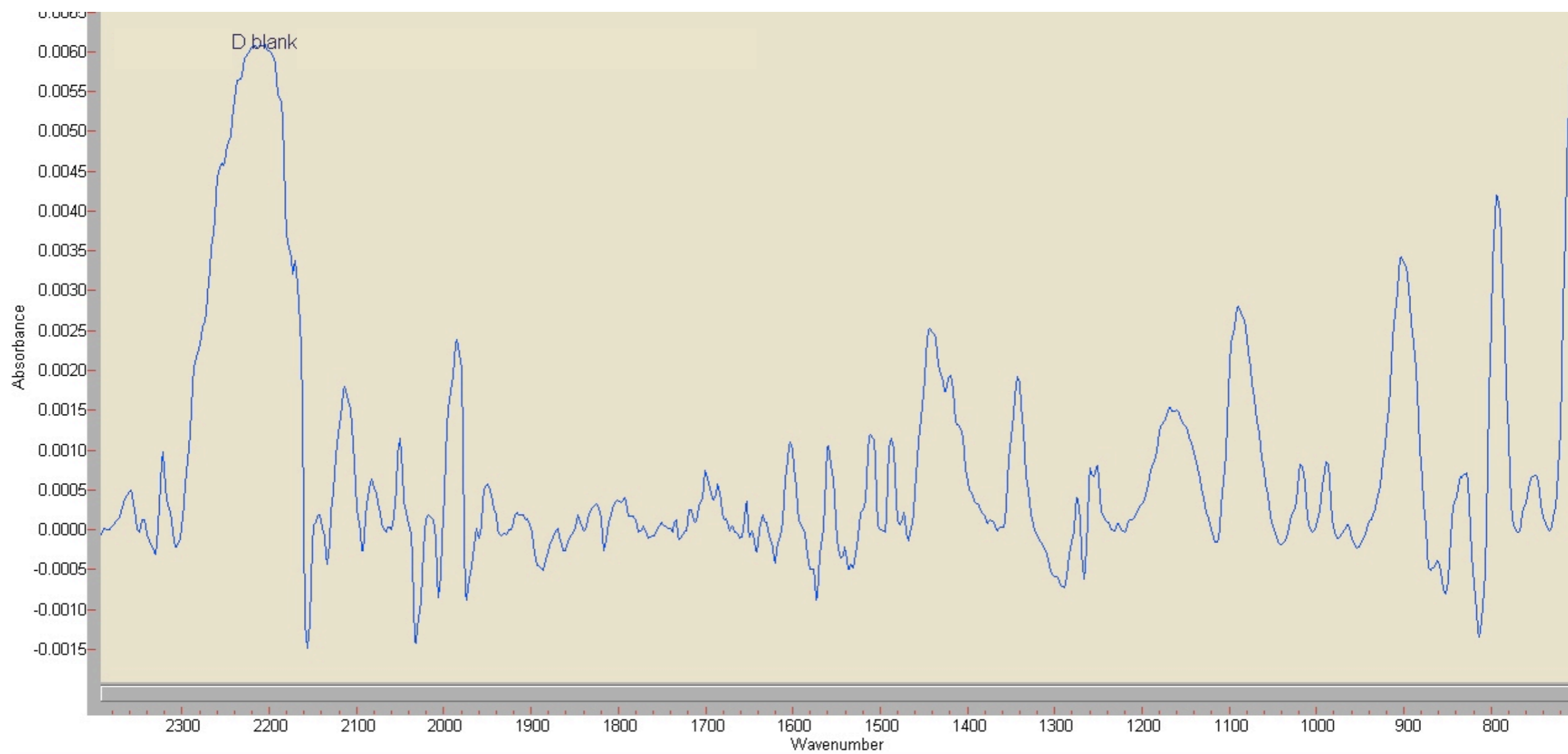
5b

# ATR-IR



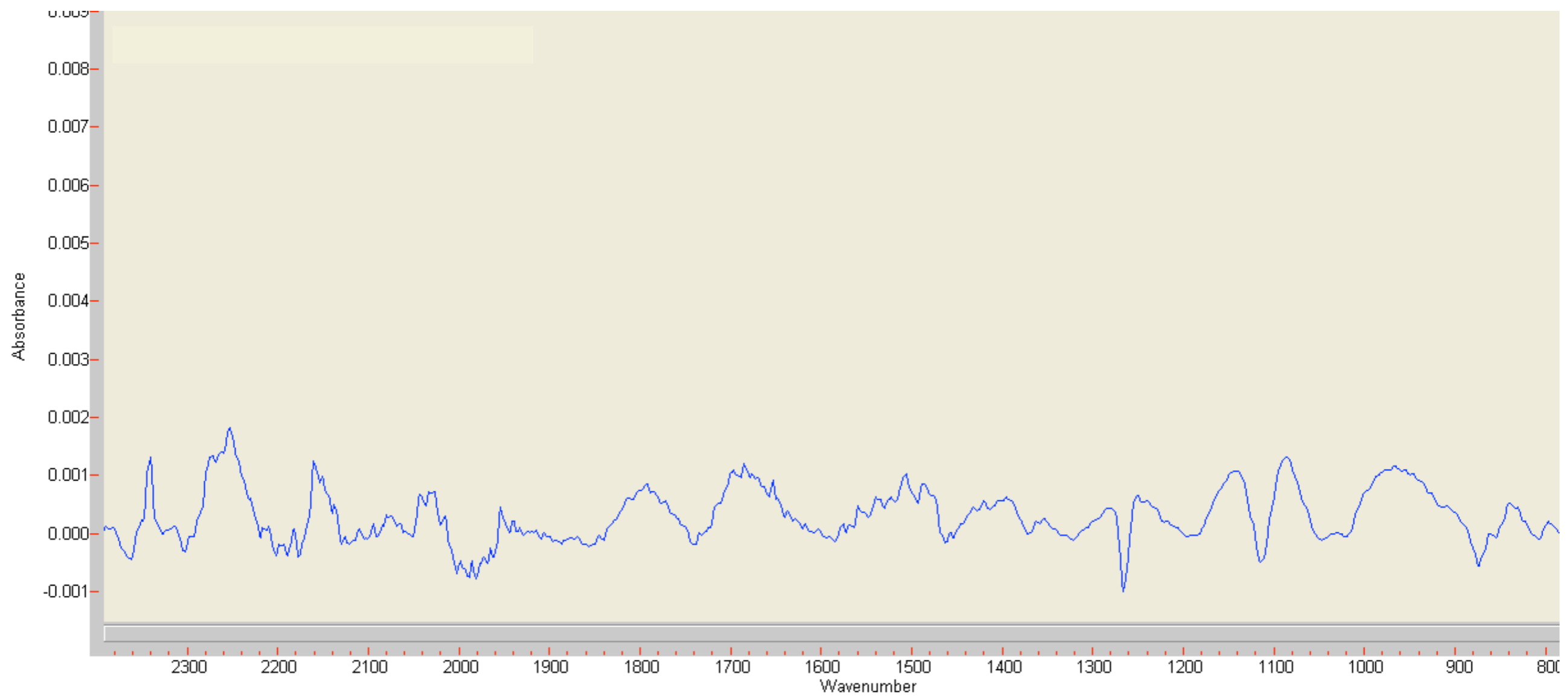
5c

# ATR-IR



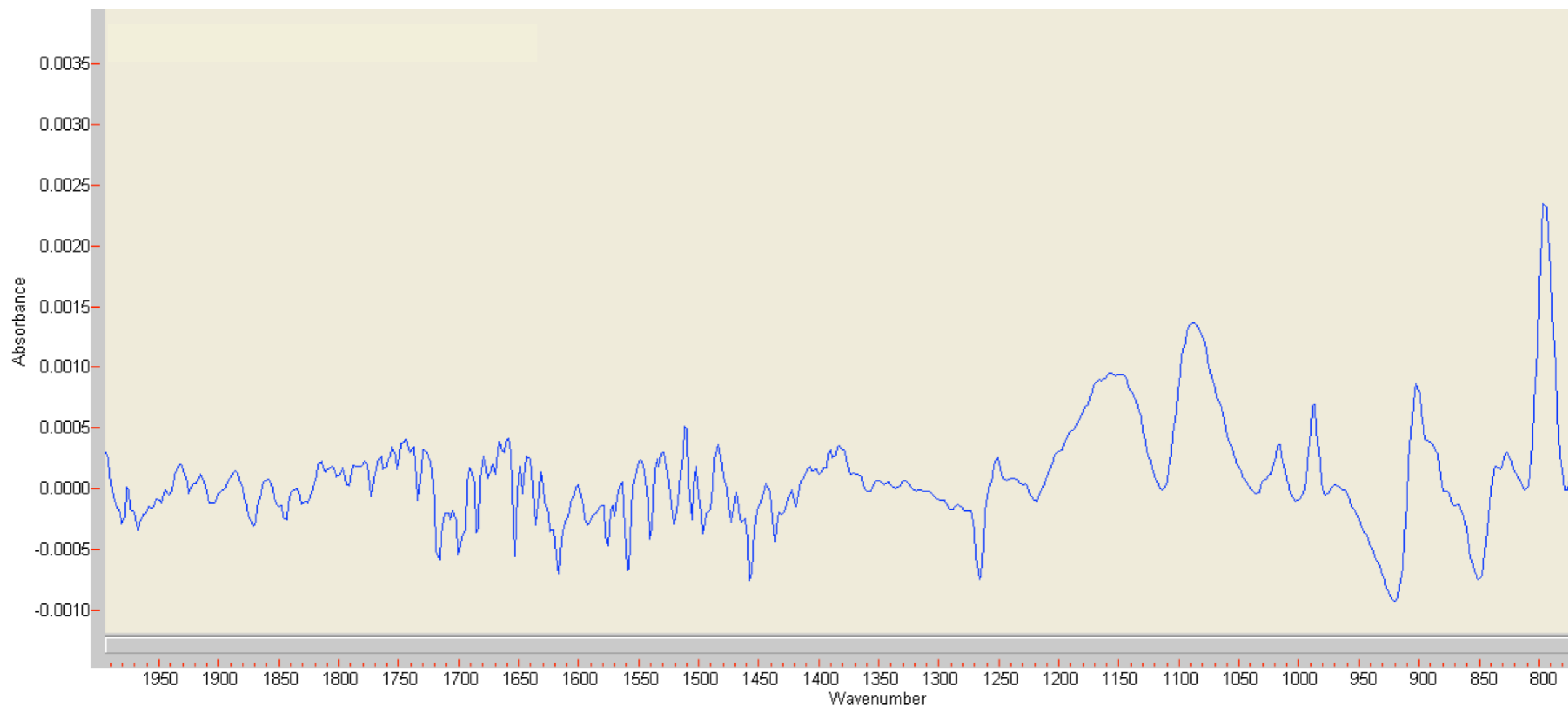
5d

# ATR-IR



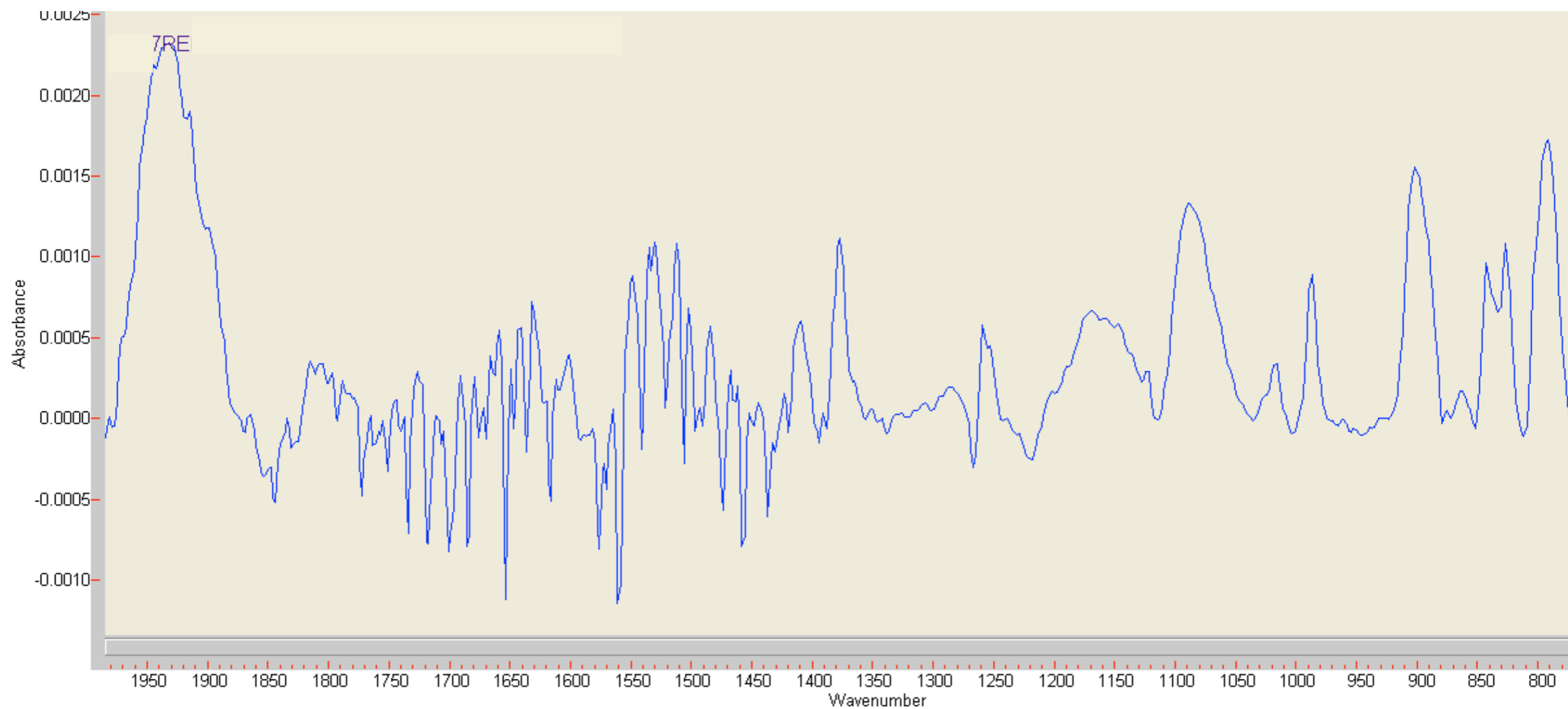
||

# ATR-IR



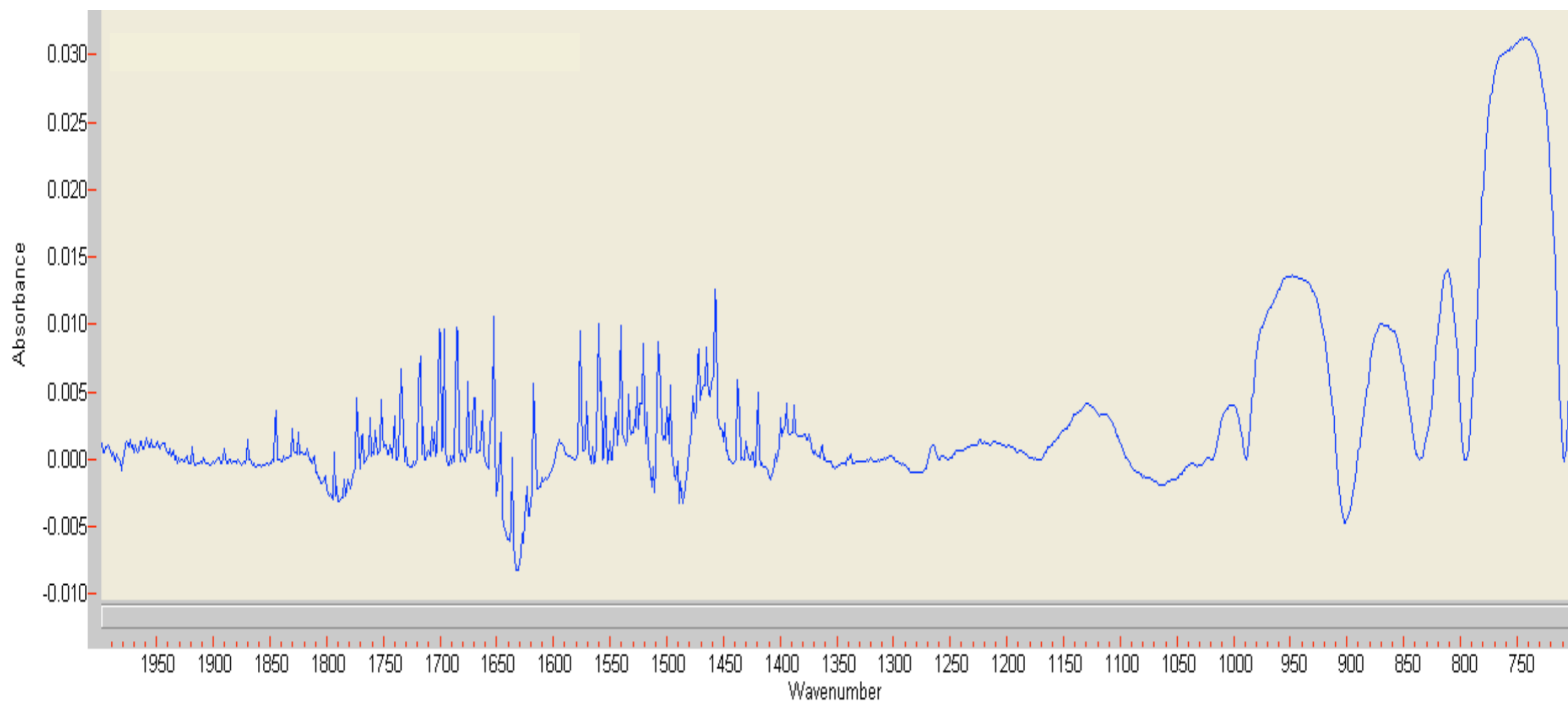
I2

# ATR-IR



# I2ATSMA

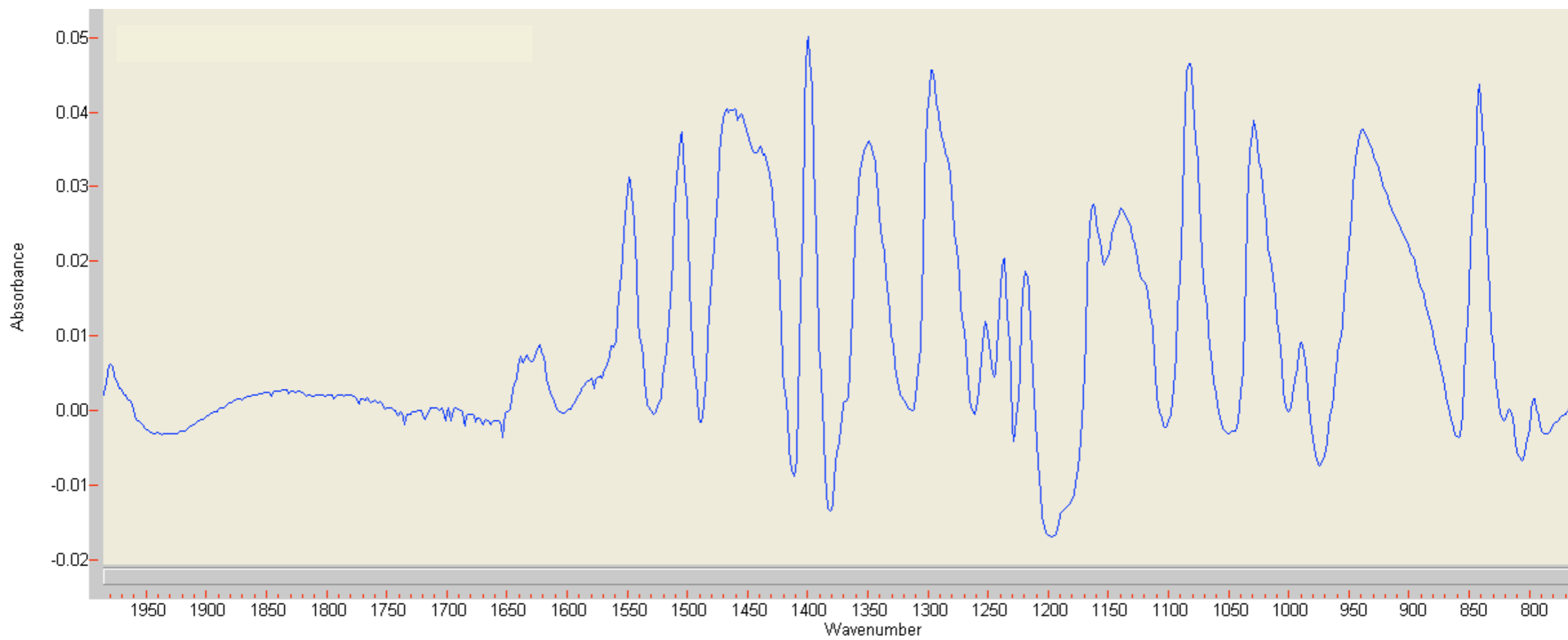
# ATR-IR



I2ATSM

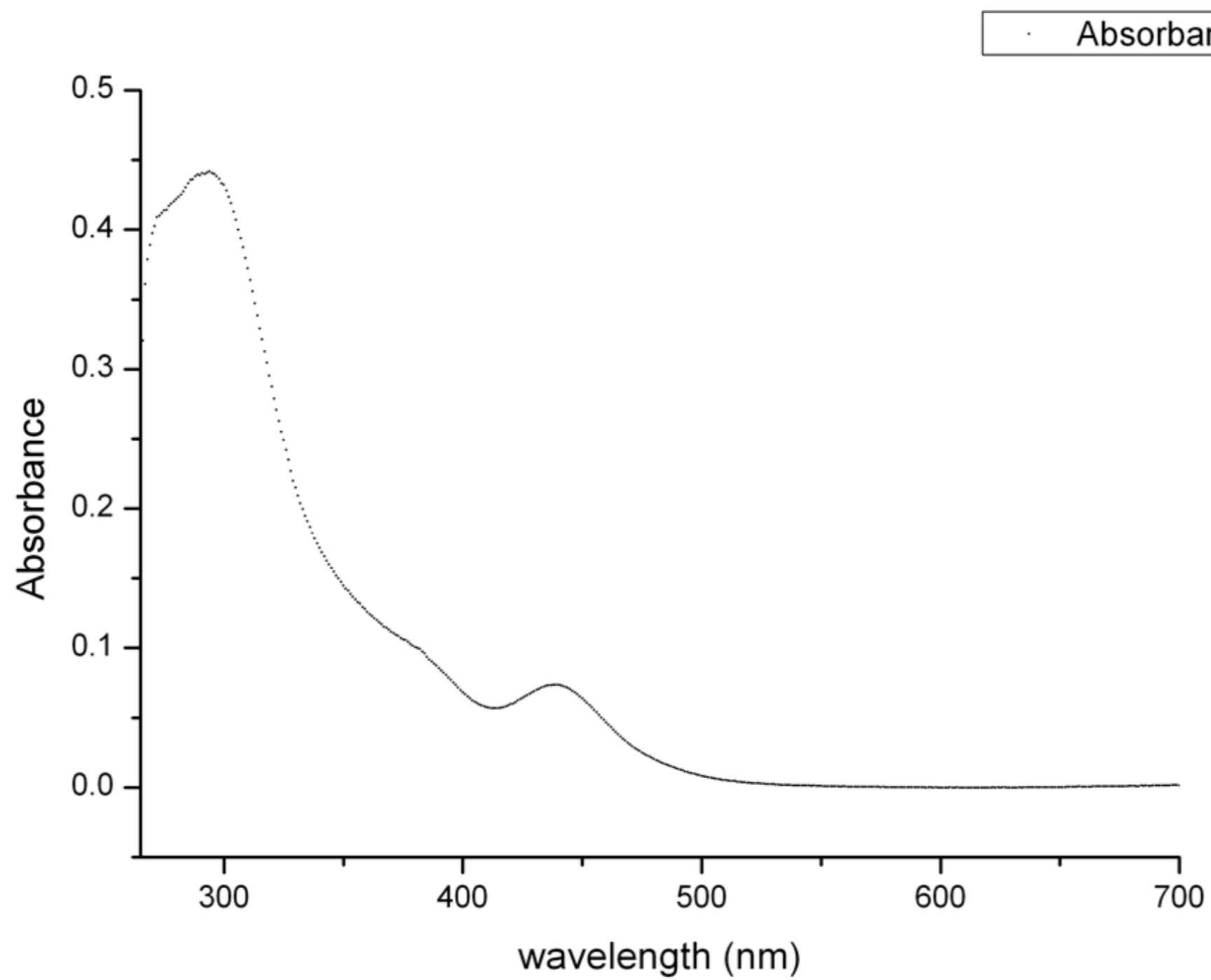


# ATR-IR



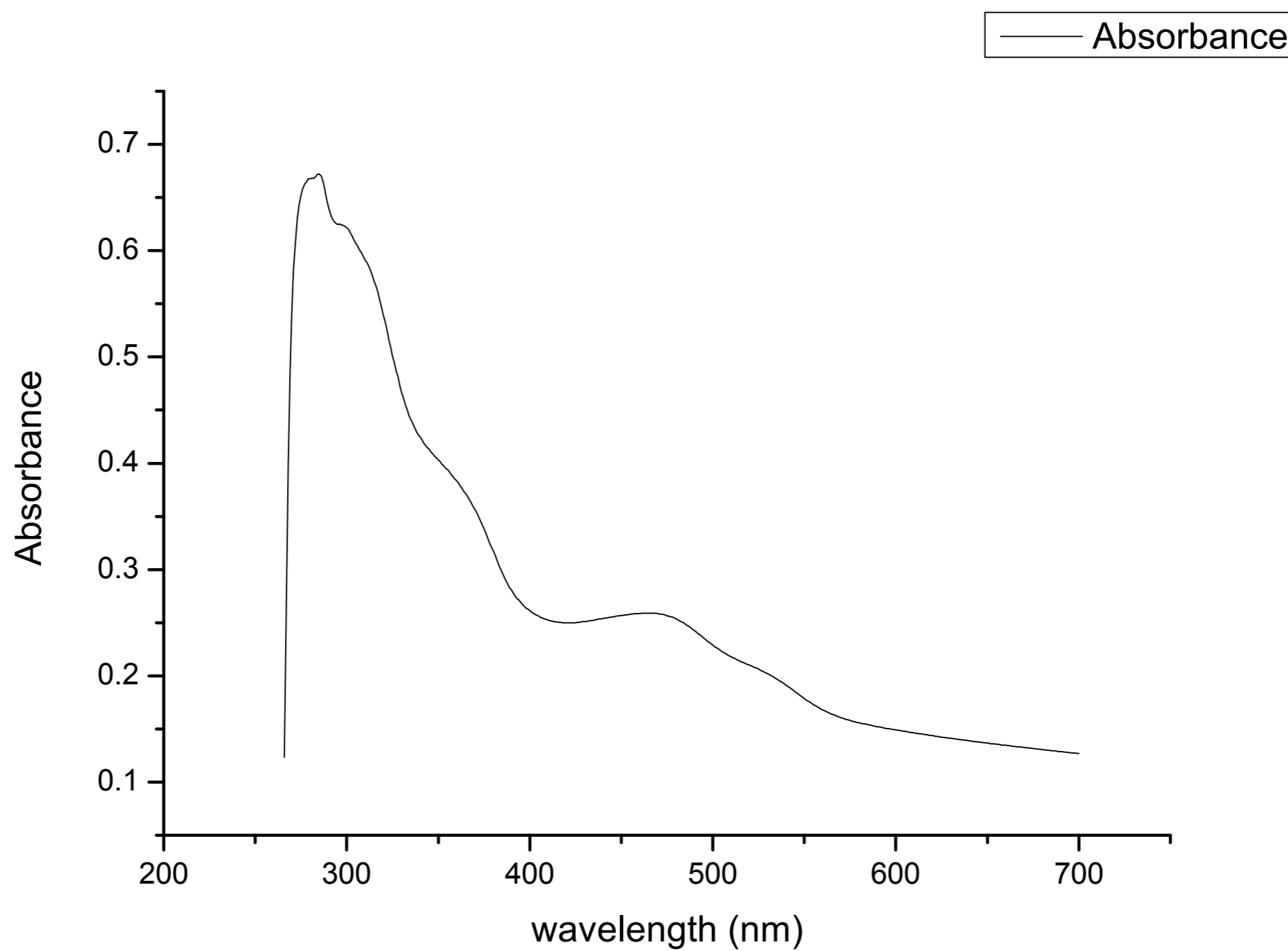
13a

# UV/Vis



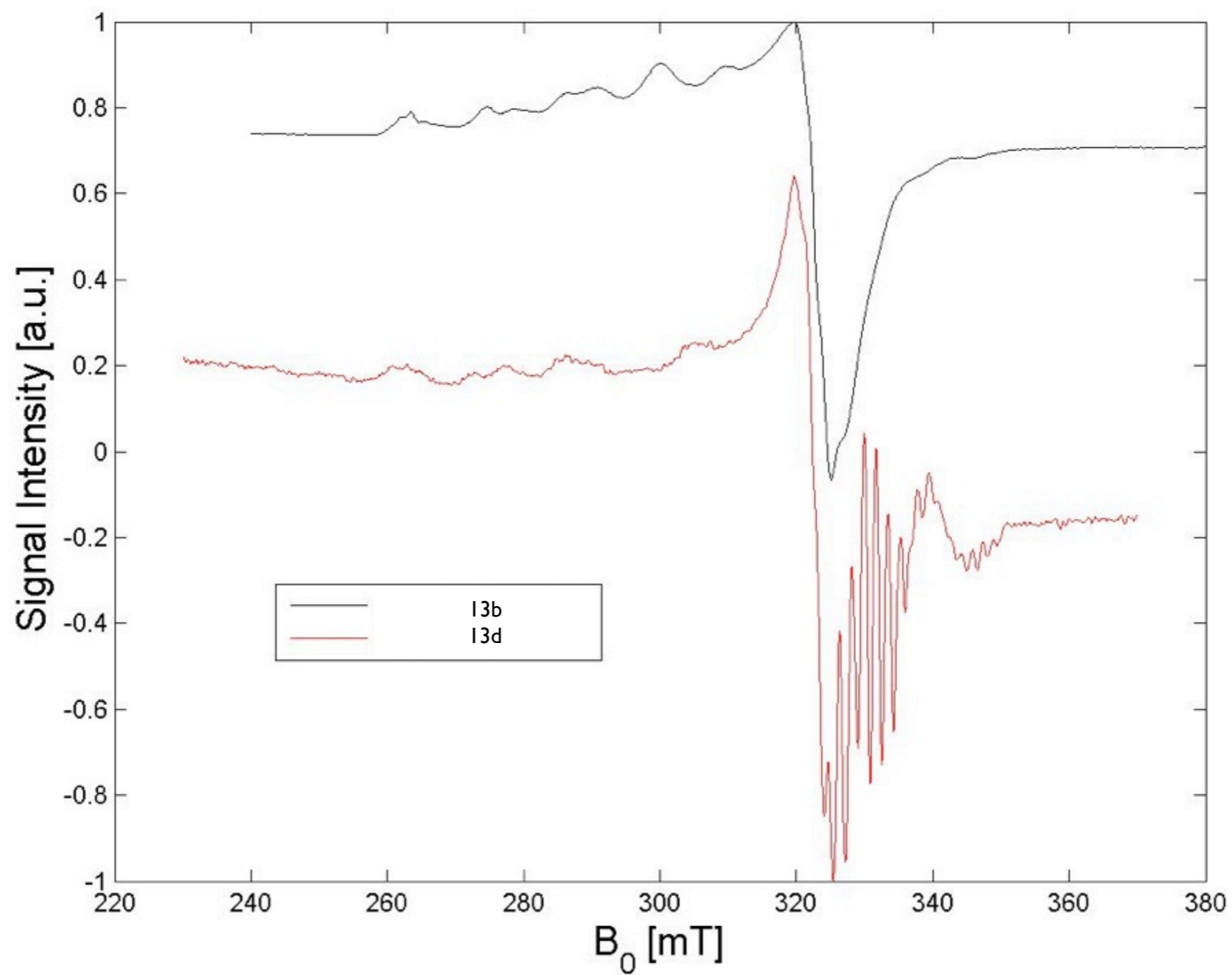
## 13b

# UV/Vis



# 13d

# EPR

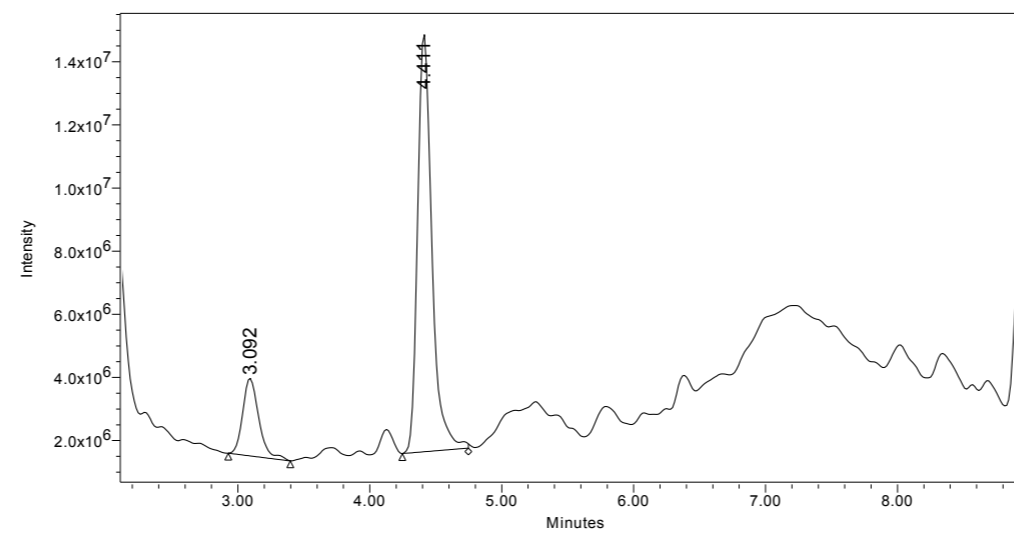
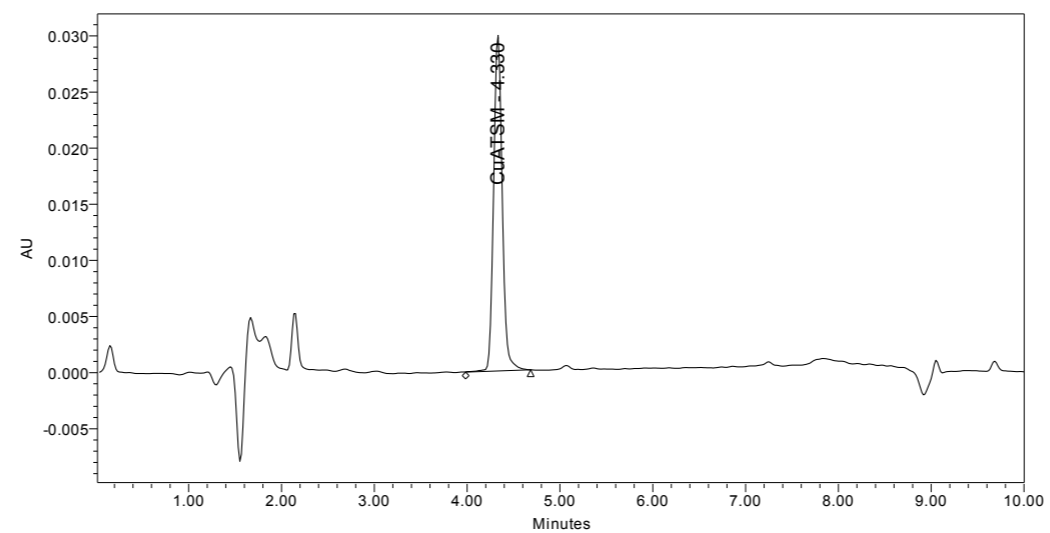


**13b, 13d**

# HPLC

Sample Name: CuATSM 080611 35-90%      Date Acquired: 08/06/2011 12:01:40 BST  
Sample Type: Unknown                      Acq. Method Set: MS\_CuATSM\_aq  
Vial: 1    Date Processed: 08/06/2011 12:19:21 BST, 08/06/2011  
Injection Volume: 5.00 ul                      Processing Method: PM\_PDA, PM\_tic  
Run Time: 10.0 Minutes                      Project Name: Copper complex

Method for measuring CuATSM                      Channel Name: 307nm, MS TIC  
Column Phenomenex Luna Phe-Hex, 150 x 3mm 3µm /30°C  
20%MeCN/MeCN, 30-90%,5/0.5ml/min/PDA/ZQ

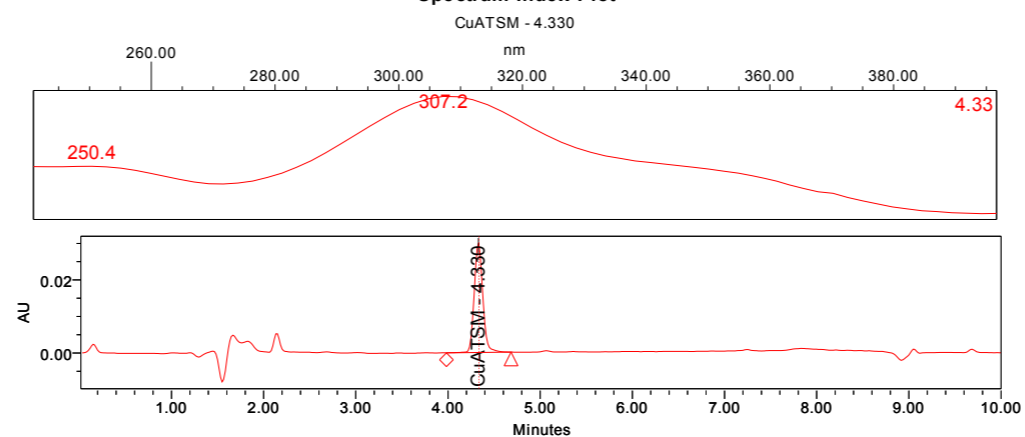


# I3d

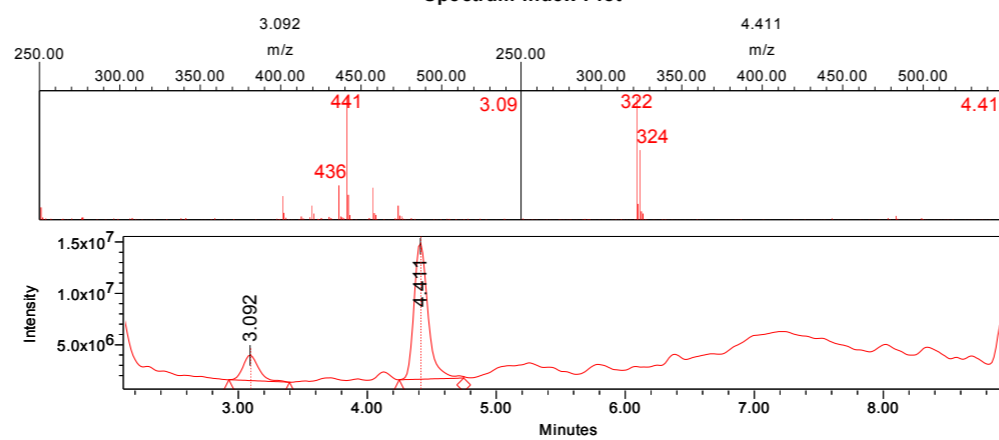
# HPLC

Peak Name	RT	Area	% Area	Height	Channel Name
1	3.092	20870308	17.26	2456793	MS TIC
2 CuATSM	4.330	194425	100.00	29822	307nm
3	4.411	100060488	82.74	13211710	MS TIC

Spectrum Index Plot

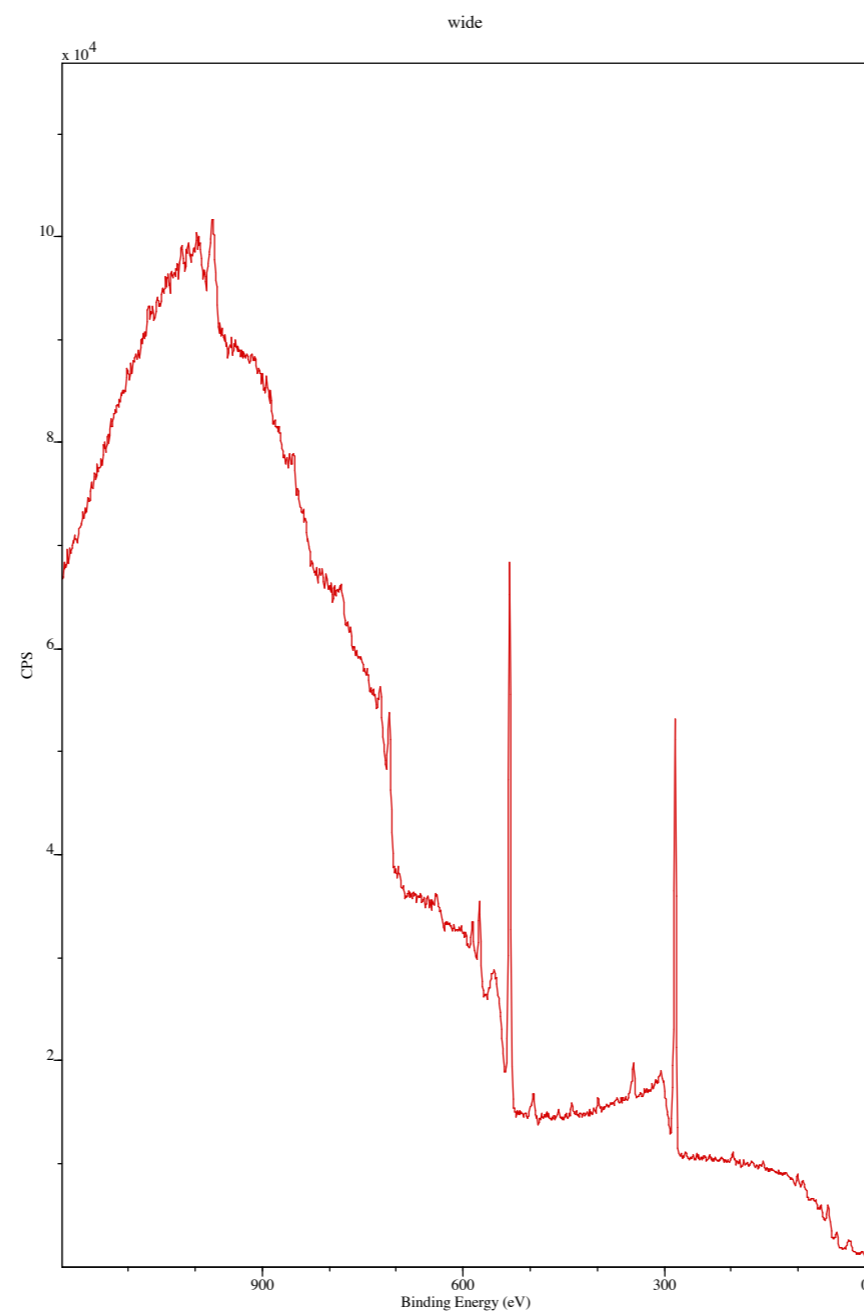


Spectrum Index Plot



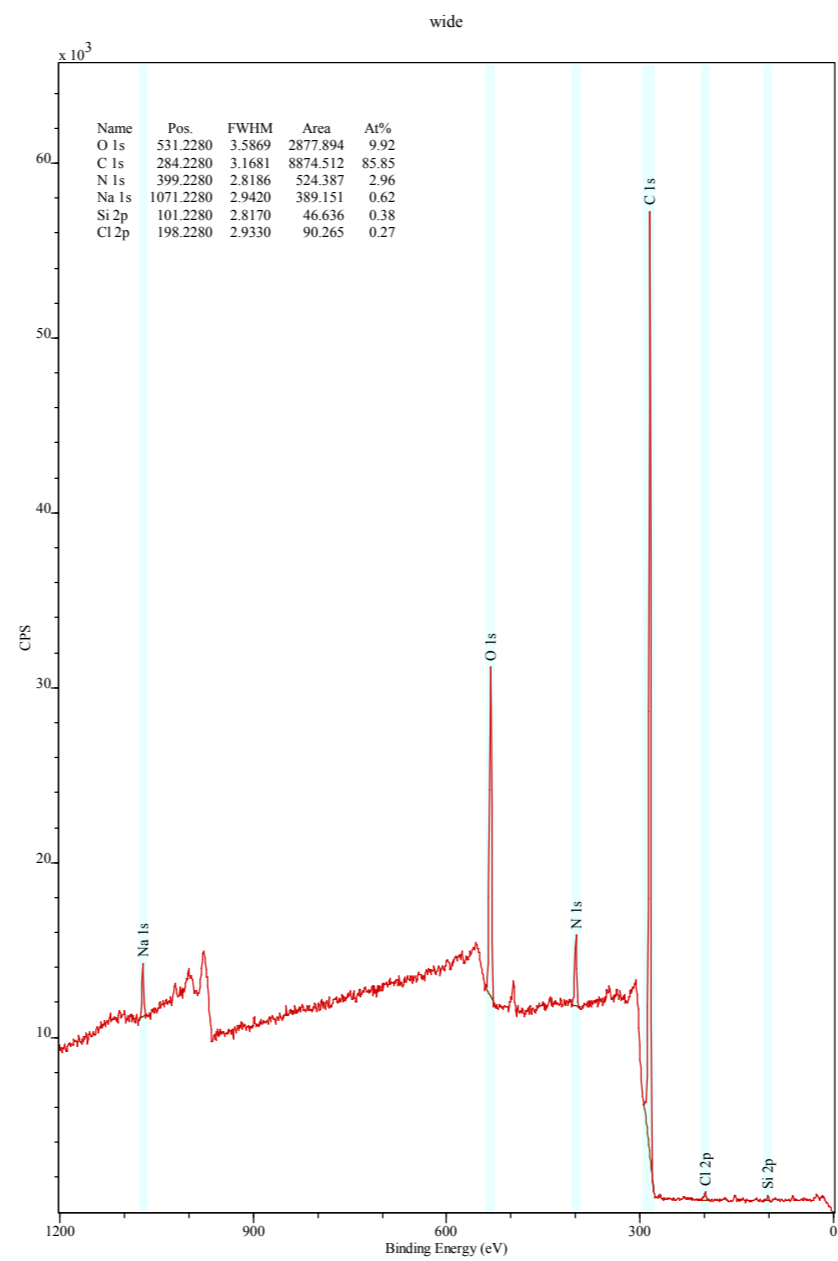
# I 3d

# XPS



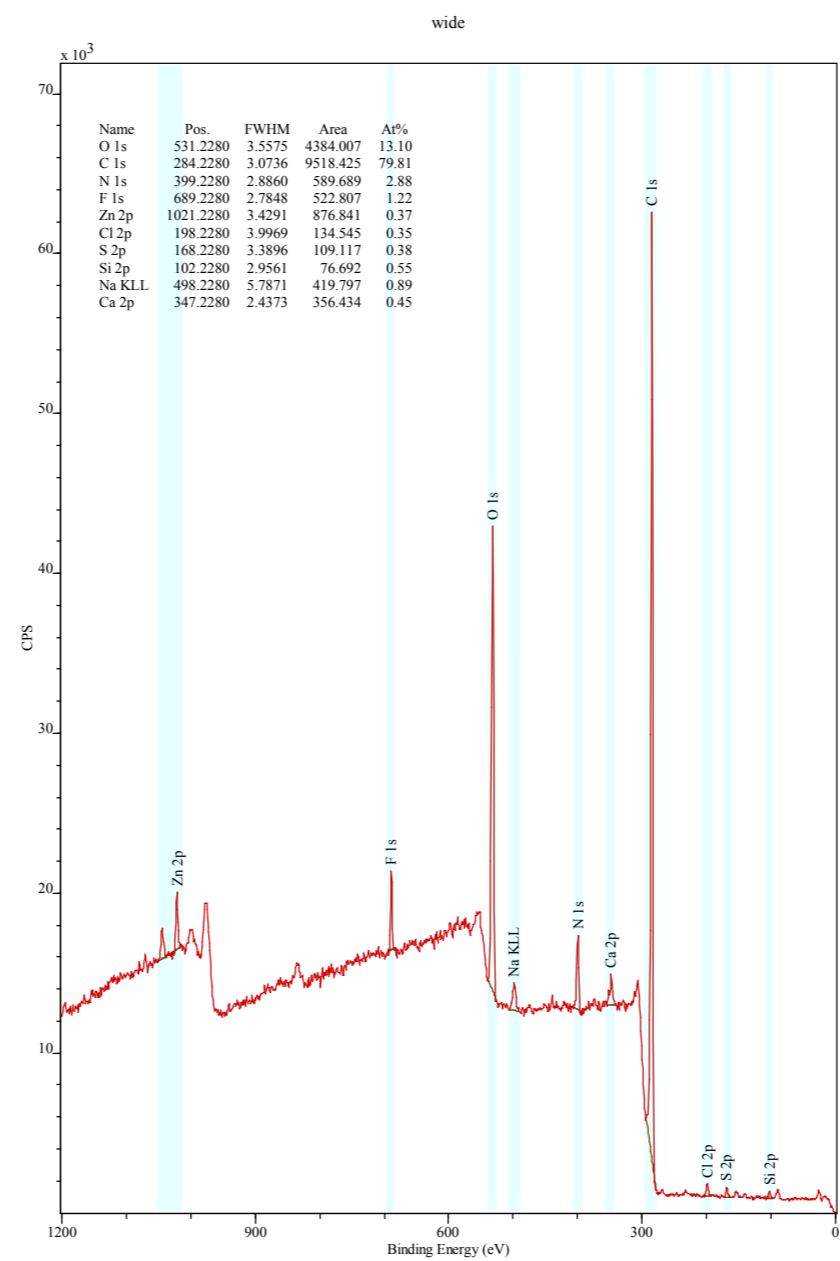
# PS XAD

# XPS



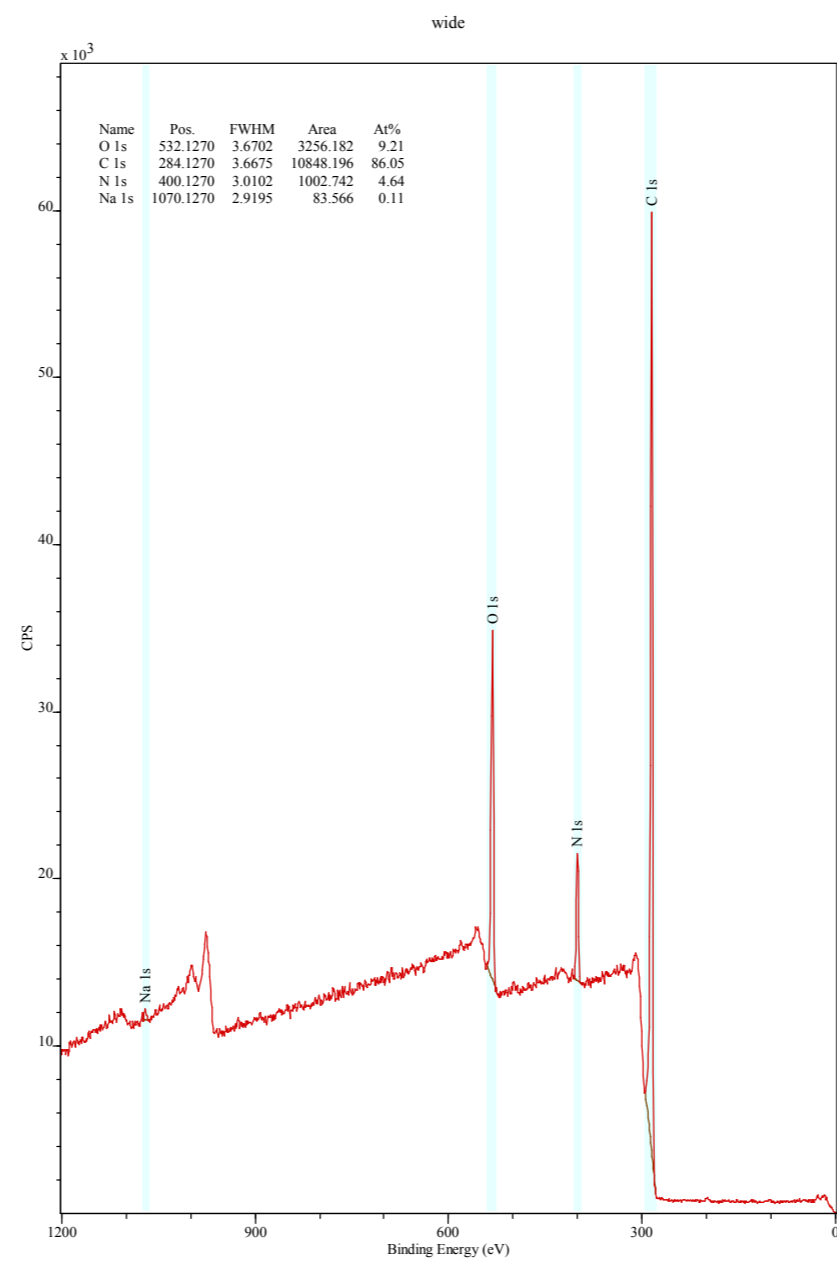


# XPS



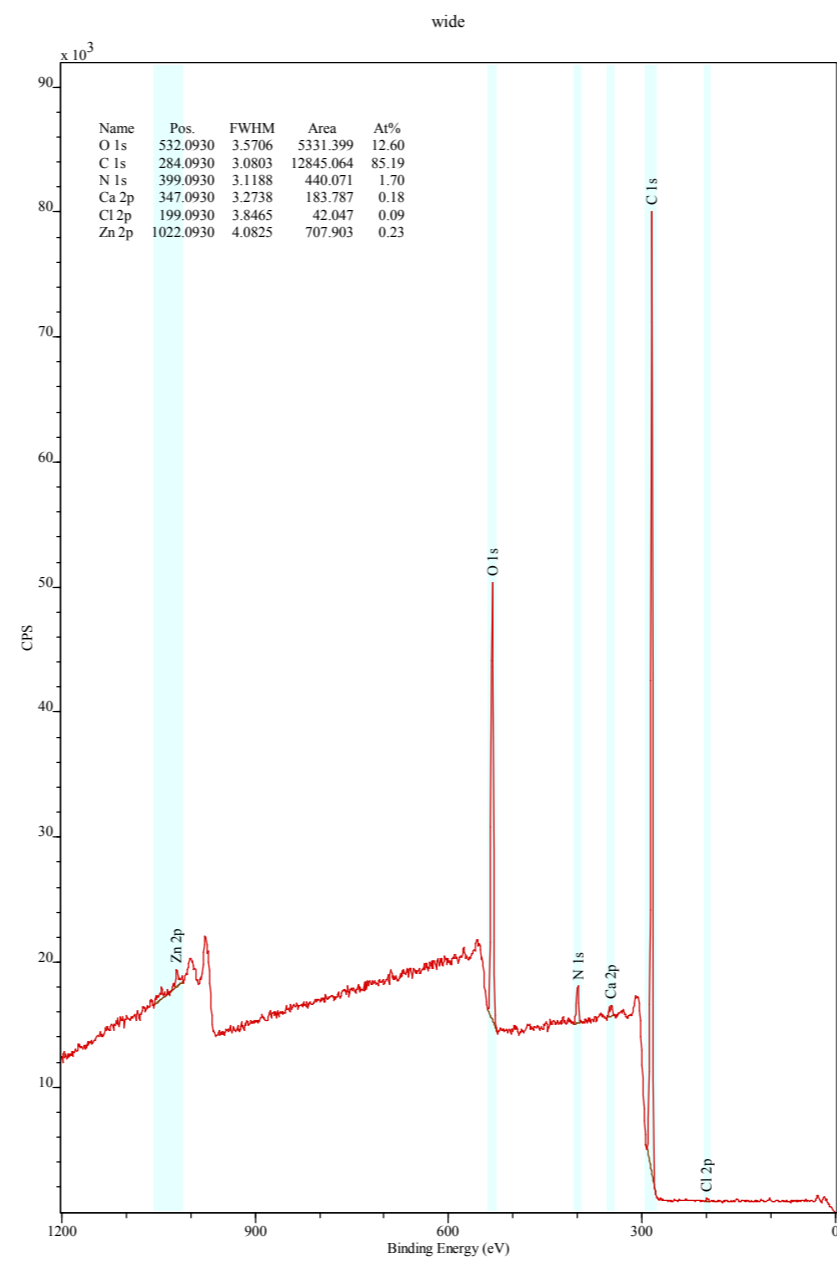
## 3Zn

# XPS



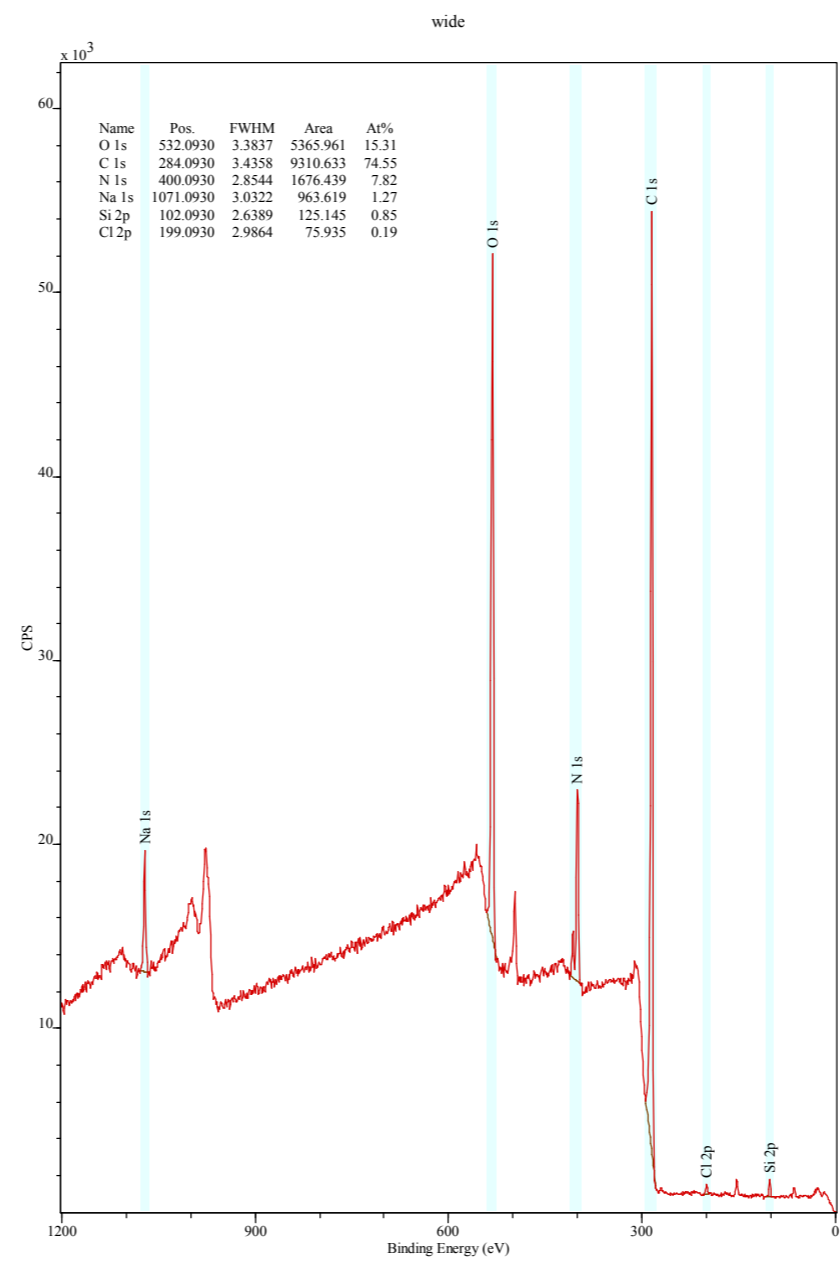
5a

# XPS



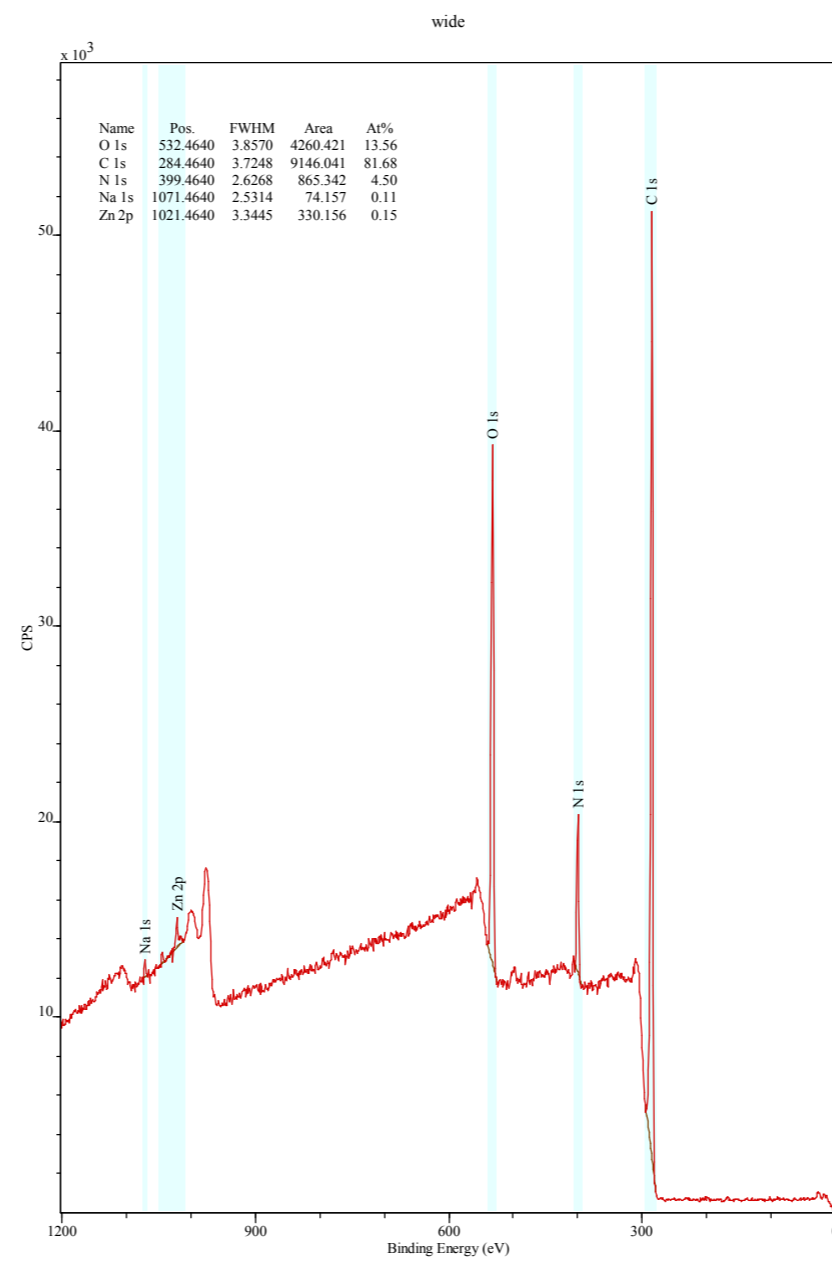
## 5aZn

# XPS



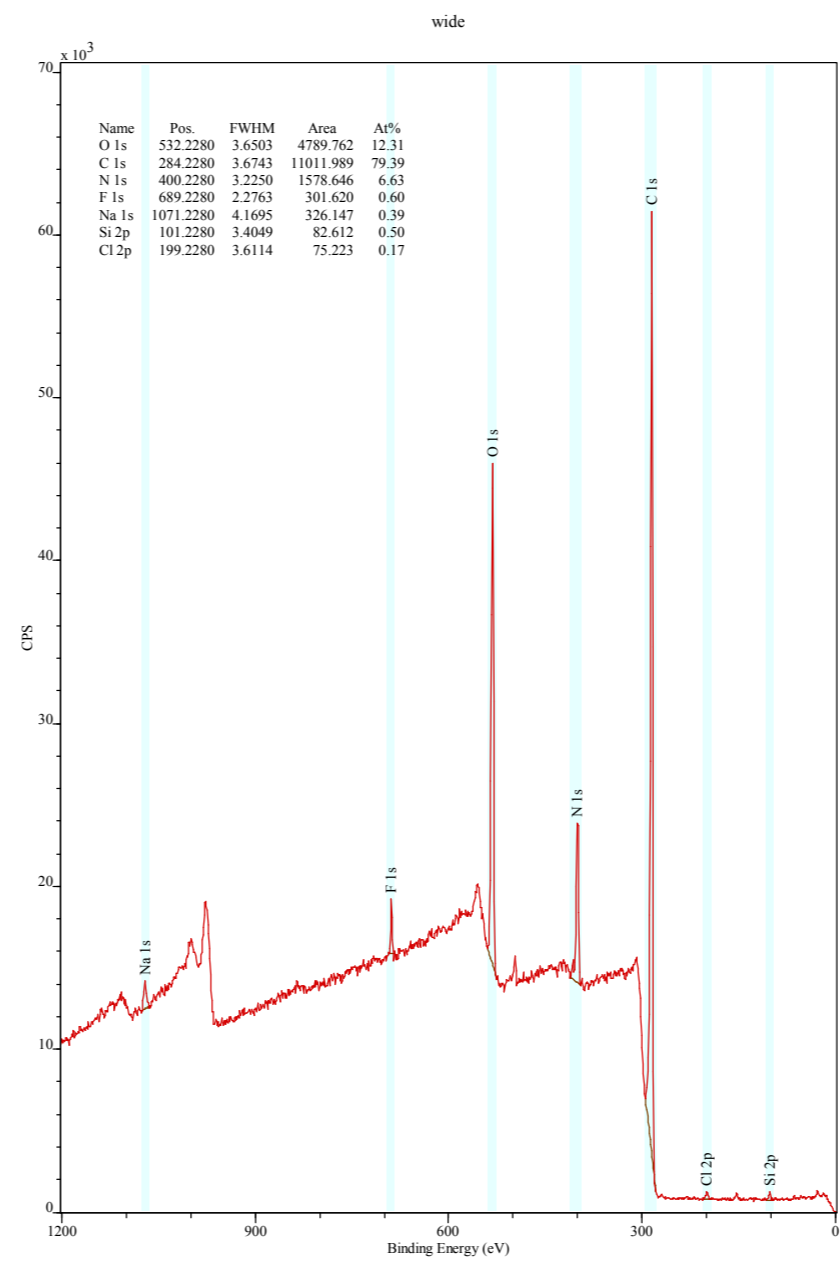
## 5b

# XPS



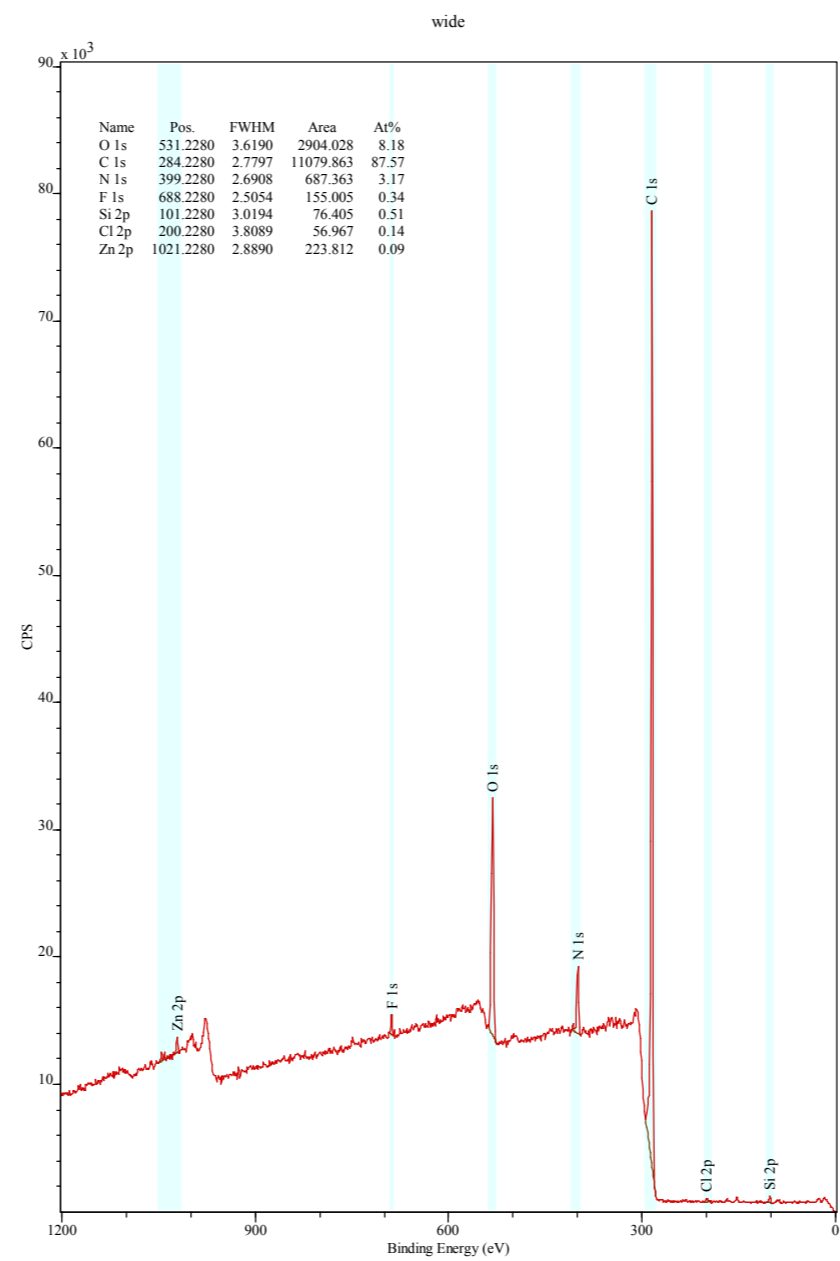
## 5bZn

# XPS



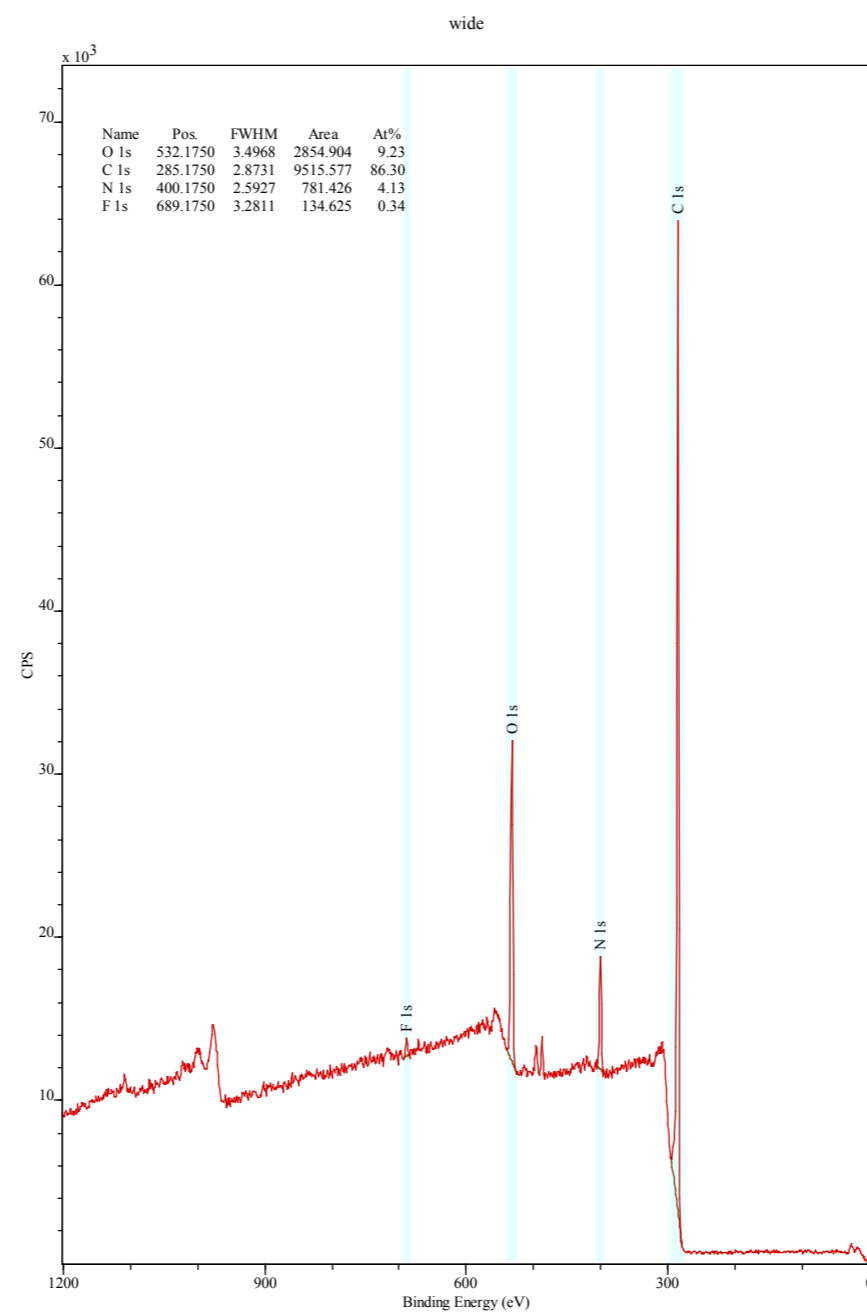
## 5c

# XPS



## 5cZn

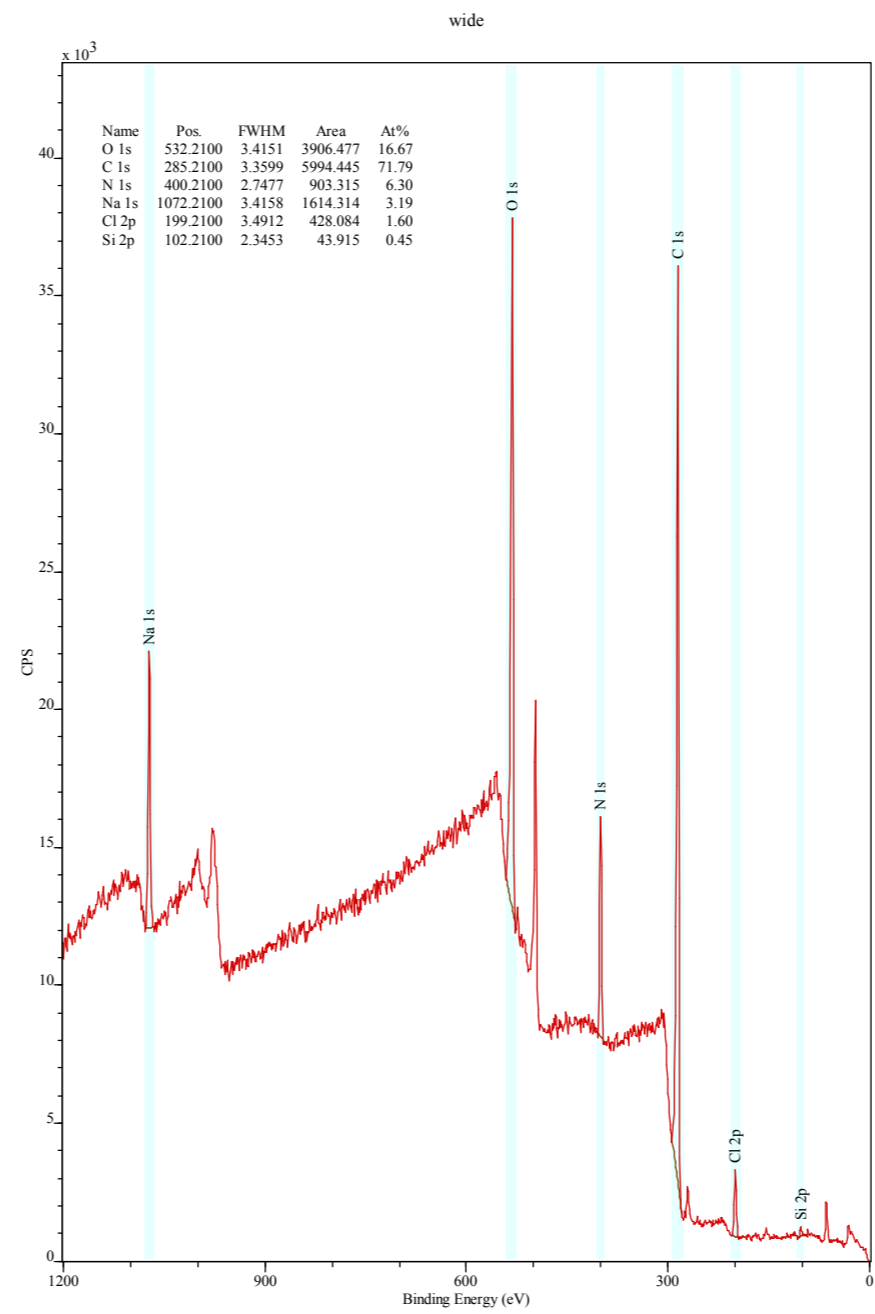
# XPS



# 5d

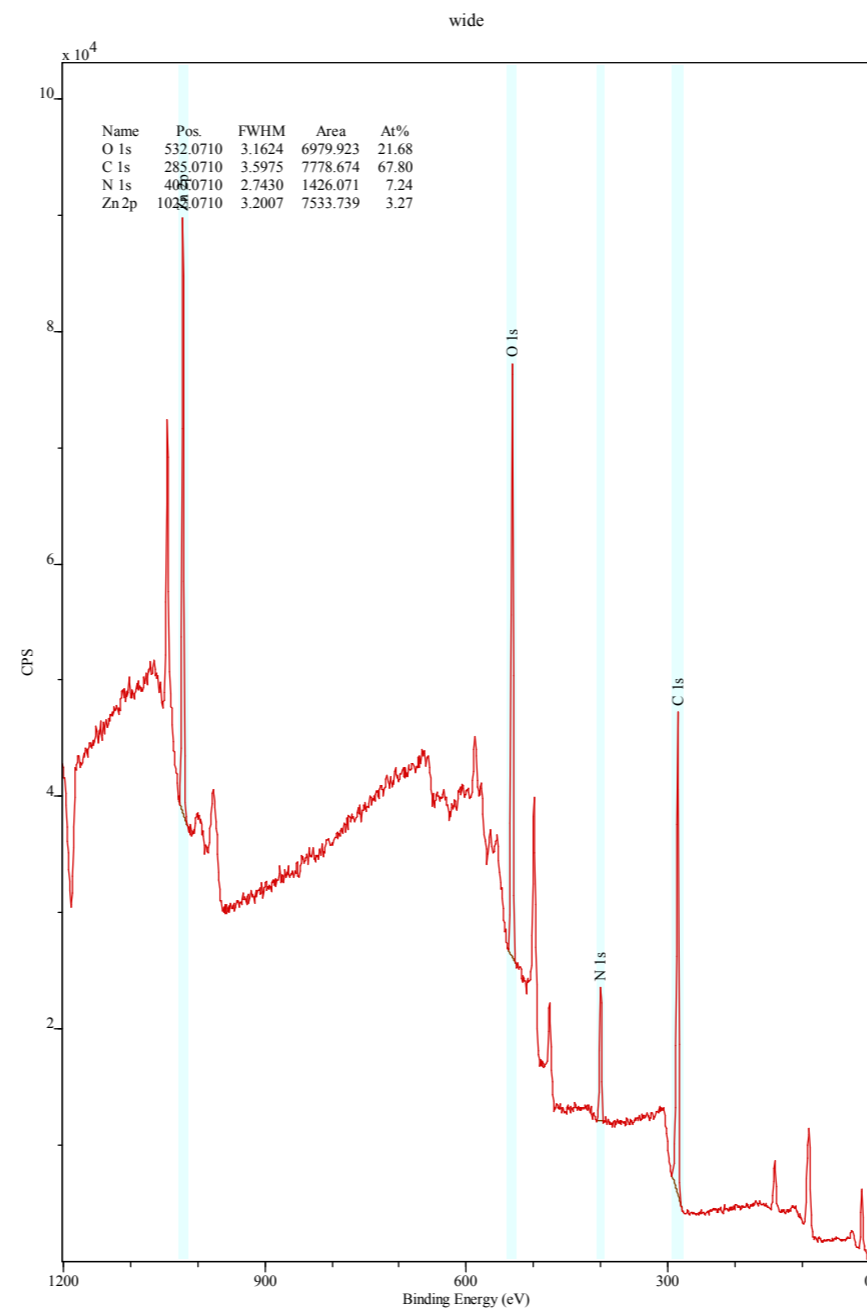


# XPS



||

# XPS

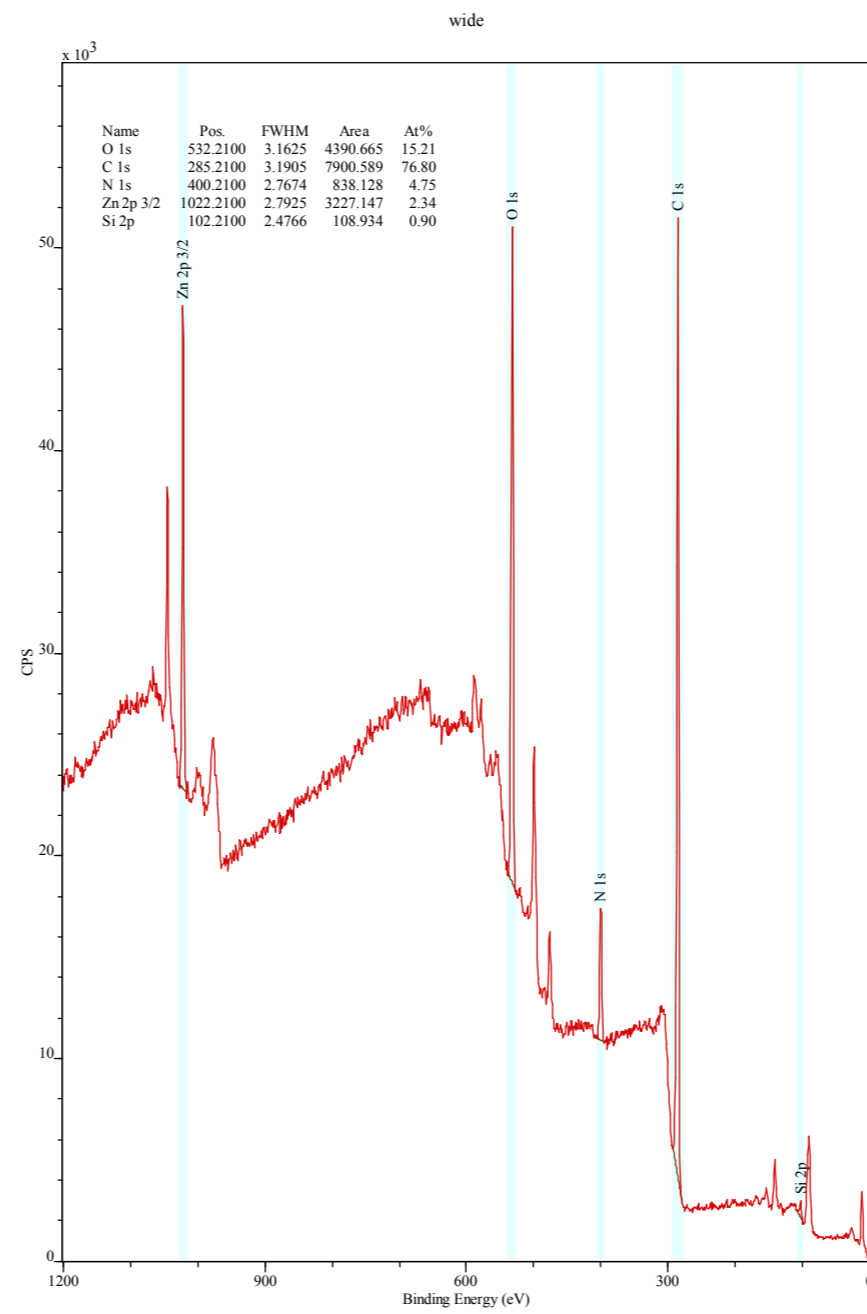


# II Zn

# XPS

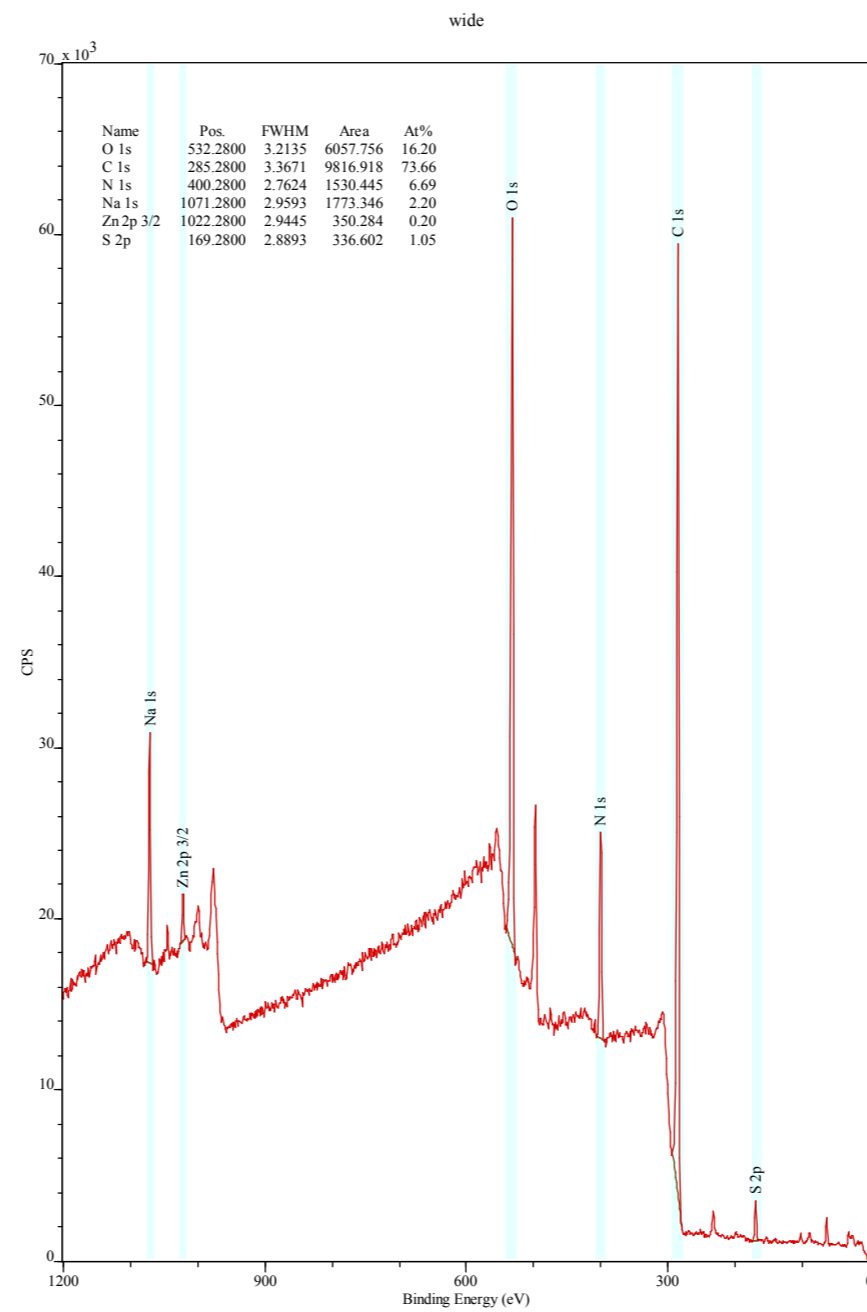


# XPS



# I<sub>2</sub>Zn

# XPS



# I2ZnATSMA